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### (54) **HIGH PERFORMANCE IMPULSE INK JET METHOD AND APPARATUS**

**HOCHLEISTUNGSIMPULS TINTENSTRAHLVERFAHREN UND GERÄT**

**APPAREIL A JET D'ENCRE IMPULSIONNEL HAUTE PERFORMANCE ET PROCEDE  
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**US-A- 4 646 106** **US-A- 4 686 539**

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## Description

### Field of the Invention

[0001] This invention relates to drop-on-demand or impulse fluid jets which eject a droplet of fluid such as ink in response energization of a transducer which may take various forms according to the preambles of claim 1 and claim 12 respectively.

[0002] US-A-4 686 539 discloses a method for driving an ink jet head, comprising the steps of producing a composite drive waveform having, for each drop of ink, at least first, second and third electrical pulses for ejecting from said ink jet head respective first, second and third ink droplets having successively higher velocities upon exit from said head, whereby said droplets merge in flight for producing an ultimate ink drop.

[0003] US-A-4 491 851 discloses a method for driving an ink jet printer which includes an electromechanical transducer which is operated by electrical pulses to eject ink from an ink nozzle connected to pressure chamber wherein two successive electrical pulses are supplied to the transducer before the ejected ink is separated from the remaining ink in the pressure chamber.

### Background of the Invention

[0004] Impulse fluid or ink jets are designed and driven so as to eject a droplet of fluid such as ink from the chamber through an orifice of the ink jet device. In many applications, it is not necessary to operate the ink jet device at high performance levels, *i.e.*, at high velocities and long throw distances. However, many applications including industrial applications require high performance ink jet devices.

[0005] For example, in various industrial ink jet applications, it is very important to eject droplets at high velocities with long throw distances so as to reach targets some distance from the ink jet orifice while maintaining a relatively small droplet size to create a high resolution dot on the target itself. In order to achieve this result, it is important that the head of the droplet as well as its tail remain attached to each other and travel at the same relatively high velocity.

[0006] In the prior art, it has been difficult to achieve high velocity and long throw distances. For example, with expanding piezoelectric transducers in ink jet print heads of the type disclosed in U.S. Patent No. 4,646,106, high performance is achieved in terms of frequency response using fluidic Helmholtz frequencies of from 25 to 50 kHz and comparable piezoelectric length mode resonant frequencies. However, the droplets formed have long tails which tend to lower the droplet velocity and the throw distance thus precluding optimum performance.

[0007] U.S. Patent Nos. 4,523,201 and 4,523,200 disclose similar print heads driven by voltage waveforms having a first pulse of longer duration and a second

pulse of shorter duration designed to achieve early break off of the droplet tail. However, the devices disclosed therein are designed to operate at Helmholtz frequencies of less than 50 kHz and there is no disclosure of the effect of exciting higher harmonic frequencies to achieve break off of the tail for producing higher velocity droplets with improved throw distance. Rather the second pulse merely improves aiming.

[0008] Reference is now made to Figs. 1A through 1F which schematically depict the drive waveform in Fig. 1A and the ink jet device itself at various points in time in Figs. 1B through 1F. Referring to Fig. 1A, the drive waveforms depicted with voltage on the ordinate and time on the abscissa. At time A, the ink jet device as depicted in Fig. 1B is maintained in the quiescent state with the transducer 10 unenergized and a predetermined volume of ink 12 contained within the chamber 14 behind an orifice 16. At time B as shown in Fig. 1A, the transducer 10 is driven by the voltage pulse 17 as shown so as to contract the length of the transducer 10 thereby increasing the volume of ink 12 within the chamber 14 and pulling back the meniscus 18 in the orifice 16 to the position shown.

[0009] As shown in Fig. 1C, which corresponds to time C of Fig. 1A, the transducer 10 begins to expand as the voltage is reduced as applied to the transducer 10. As a result, the volume of ink 12 within the chamber 14 begins to contract while advancing the meniscus 18 through the orifice 16 as shown in Fig. 1D. At a slightly later time than C but before D as shown in Fig. 1E, the transducer 10 has nearly returned to the quiescent state as shown in Fig. 1E and a droplet 20 with a ligament 21 has begun to form at the orifice 16. In Fig. 1F which corresponds to time D in Fig. 1A, the droplet 20 has traveled some distance from the orifice 16 with a slowly moving tail 22 attached. As depicted in Fig. 1F, the tail 22 has just broken off from the meniscus 18 at the orifice 16 before the volume of ink within the chamber 14 returns to the condition shown in Fig. 1B. As can be readily seen from Fig. 1F, the tail 22 is elongated in a manner so as to create a "lay over" condition on a target assuming the tail 22 and the head 20 remain attached throughout their flight to the target. Tail 22 which is relatively slow moving as compared to the head velocity which makes the tail grow in length and break up thereby decreasing the overall throw distance to the target.

[0010] In the devices of the prior art of the type disclosed in U. S. Patent Nos. 4,459,601, 4,509,059, 4,646,106 and 4,697,193, ink jet devices have been characterized by Helmholtz resonant frequencies of approximately 40 kHz and piezo length mode resonant frequencies of 45 kHz. The tail which was formed at the meniscus saw pressure disturbances of approximately 45 kHz. As a consequence, the tail would be broken off as shown in Fig. 1F in response to this disturbance during the negative velocity part of the cycle so as to provide a very low acceleration component thereby producing a drop with a high head velocity and low tail velocity and

a tail that grows longer over long print gaps producing poor print quality.

### Summary of the Invention

**[0011]** In accordance with this invention, a high performance fluid jet method and apparatus is provided wherein high velocity droplets are ejected from the fluid jet device.

**[0012]** In further accordance with the invention, a high performance fluid jet method and apparatus are provided wherein the droplets have a large throw distance to the target.

**[0013]** In further accordance with the invention, the method of operating an impulse fluid jet device is provided wherein the device comprises a chamber and an orifice for ejecting droplets from the chamber and a transducer having a resonant frequency and a higher harmonic frequency. The method comprises the steps of generating one energy pulse of one duration coupled to the transducer for exciting the resonant frequency of the transducer. Droplet ejection is initiated such that the droplet has a head and a tail attached in response to the one energy pulse. Another energy pulse of another duration is also generated and coupled to the transducer, the other energy pulse having substantially shorter duration than the one energy pulse for exciting a higher harmonic frequency. The attached tail is broken off from the head of the droplet in response to the other energy pulse. As a result, the head and the remainder of the tail travel together toward a target.

**[0014]** In one preferred embodiment of the invention, the other pulse follows the one pulse in time. In another preferred embodiment of the invention, the other pulse precedes the one pulse in time.

**[0015]** In accordance with another important aspect of the invention, the droplet of fluid or ink including the head and the attached tail comprise at least 20 picoliters and preferably more than 60 picoliters, preferably travel at a velocity in excess of 6 meters per second, and preferably have a travel distance or throw distance of at least 0.25 inches and preferably more than 0.5 inches.

**[0016]** In accordance with a further important aspect of the invention, the transducer has a resonant frequency in excess of 50 kHz and preferably in excess of 75 kHz and a higher harmonic in excess of 150 kHz and preferably in excess of 200 kHz.

**[0017]** In accordance with another important aspect of the invention, the fluid or ink jet chamber is of a volume so as to preferably have a Helmholtz frequency in excess of 50 kHz.

**[0018]** In the preferred embodiment, the duration of the one pulse is greater than 5 microseconds but less than 100 microseconds and the duration of the other pulse is greater than .5 microseconds but less than 6 microseconds. The time delay between the one pulse and the other pulse is greater than 1 microsecond but less than 5 microseconds.

### Brief Description of the Drawings

#### [0019]

- 5 Figs. 1A through 1F are diagrammatic, partially schematic representations of the prior art as discussed above.
- Fig. 2A is a waveform for driving a fluid or ink jet device in accordance with the invention.
- 10 Fig. 2A' is an alternative waveform for driving a fluid or ink jet device in accordance with another preferred embodiment of the invention.
- Fig. 2B is a partially schematic representation of a fluid or ink jet device in accordance with this invention being driven by the waveform of Fig. 2A or Fig. 2A' as the droplet emerges from the ink jet device.
- 15 Fig. 2C is a partially schematic representation of a fluid or ink jet device which represents the device of Fig. 2B at a slightly later point in time.
- 20 Fig. 3 is a partially schematic/block diagram of an jet printing apparatus which may be utilized in practicing the invention;
- Fig. 4 is an alternative voltage waveform which may be used in another embodiment of the invention;
- 25 Fig. 4a is yet another alternative waveform which may be used;
- Fig. 5 is a circuit diagram depicting a resistor in series with a length mode piezoelectric electric transducer driven by the signal generator of Fig. 3 using the various waveforms contemplated by this invention; and
- 30 Fig. 6 depicts the resonant frequency of the transducer and a higher harmonic superimposed on drive waveforms which achieve a droplet having a high velocity with a long throw distance.
- 35

### Detailed Description of the Preferred Embodiments

- [0020]** Reference will now be made to Fig. 2A wherein a piezoelectric transducer voltage drive waveform is shown in accordance with one preferred embodiment of the invention. One pulse 23 after time A and between times B and C is generated and applied to the piezoelectric transducer so as to contract the transducer as shown in Figs. 1B and 1C. However, unlike the prior art voltage waveform of Fig. 1A, another pulse of shorter duration immediately follows the one pulse beginning at time E and terminating at time F. In accordance with this invention, the one pulse between times B and C excites the piezo resonant frequency, while the other shorter pulse between times E and F excites a higher harmonic frequency of the piezoelectric transducer. This higher harmonic frequency has a high acceleration component and enough amplitude to disturb the tail formation seen in the prior art representation of Fig. 1F as will now be described with reference to Figs. 2B and 2C.
- 40
- 45
- 50
- 55

**[0021]** As shown in Fig. 2B, the pulse 23 between times B and C forces the droplet 20 connected to the ink

12 within the chamber 14 outwardly from the orifice 16 similar to that shown in the prior art Fig. 1E. However, the shorter pulse 25 between times E and F as shown in Fig. 2A excites a higher harmonic of the piezo resonant frequency so as to interrupt the formation of an elongated tail from the ligament 22 as shown in Fig. 2B creating a more nearly spherical droplet 20 as shown in Fig. 2C with only an abbreviated tail 22 as contrasted with the elongated tail 22 shown in Fig. 1F.

**[0022]** In accordance with this invention, the piezoelectric transducer 10 is chosen so as to have a high resonant frequency. The resonant frequency of the transducer 10 is in excess of 50 kHz and preferably greater than 75 kHz with 90-300 kHz being preferred and representing the preferred embodiment. The higher harmonic frequency which is excited by the trailing pulse between times E and F is in excess of 150 kHz with frequencies in excess of 200 kHz preferred and 235 kHz utilized in the preferred embodiment. For the preferred embodiment where the resonant frequency is 90-300 kHz and the higher harmonic is 235-800 kHz, the pulse 23 between times B and C is preferably 14.5 microseconds which pulls the ink back in the meniscus 18 to the position shown in prior art Figure 1C. The pulse 23 between times B and C is followed by a dead time between time C and E which is preferably 1.5 microseconds followed by the shorter pulse 25 between times E and F of 3.0 microseconds in duration so as to excite the higher harmonic of 235 kHz. This higher harmonic resonant of frequency of 235 kHz creates a pressure wave with a high acceleration component that disturbs the ink flow in the orifice as the ink flows out as discussed above. Tail formation as a consequence is greatly affected such that the tail breaks off from the meniscus 18 much earlier than in the single pulse approach of the prior art. The shorter tail 22 can now travel with the head of the drop 20 because the liquid surface tension is now high enough to keep the drop together and accelerate the shorter tail to the same velocity as the head of the drop.

**[0023]** In accordance with another important aspect of the invention, increasing the fluidic resonant frequency improves throw distance of the drops. For example, increasing the fluidic resonant frequency or Helmholtz frequency from 45 kHz to 90 kHz and correspondingly increasing the natural ringing frequency of the transducer from 45 kHz to 90 kHz can in of itself increase the drop tail velocity from 4.5 meters per second to 5.5 meters per second with the head traveling at 6.5 milliseconds so as to increase the throw distance of the drop at least 75 percent. With the addition of another pulse with a short duration so as to excite the higher harmonic resonant frequency such as for example 235 kHz, the tail of the drop may be broken off sufficiently earlier so as to increase the tail velocity to 6.5 to 7 meters per second. This produces ink drops with throw distances increased by as much as 200 percent.

**[0024]** It will be appreciated that the same higher harmonic frequencies which achieve early droplet break off

and shorter tails may be achieved by the use of a shorter pulse before or after a longer pulse. As shown in Fig. 2A', a shorter pulse 27 between times G and H precedes the longer pulse between times B and C. The effect is the same since the shorter pulse 27 following the longer pulse 23 is capable of exciting the higher harmonic frequency, i.e. a frequency in excess of 150 kHz and as high as 235 kHz in the preferred embodiment.

**[0025]** Referring to Fig. 3, a system is shown including a plurality of fluid or jet devices of the type shown in Fig. 2B and 2C incorporated in a head 24 with orifices 16 shown of exaggerated size. The head 24 is driven by a signal generator 26 connected to a power supply 28 and a voltage regulator 30. A timing circuit 32 is coupled to the signal generator so as to generate voltage drive pulses for the transducers of the fluid or ink jet devices incorporated in the head 24 which include a longer pulse of the type described above as well as a shorter pulse which may precede or follow the longer pulse.

**[0026]** As shown in Fig. 3, a droplet 20 is being ejected in a direction indicated by the arrow 34 toward a target or object 36 carried by a conveyor 38. In many applications, it may be desirable or necessary to separate the head 24 from the target 36 by some distance. It is therefore important to achieve long throw distances and high drop velocity with little or no tail in order to achieve high resolution drop and accuracy in accordance with this invention.

**[0027]** It should also be appreciated that the invention is not limited to any particular type of wave shape. As shown in Fig. 4, the wave shape need not be square or rectangular but may be almost sawtoothed and the voltage level between the longer pulse 37 and the shorter pulse 39 need not go to zero but need only to have a substantially lesser amplitude than the peaks of the longer pulse and the shorter pulse. In this regard, the longer pulse 37 between times I and J shown in Fig. 4 is almost triangular as is the shorter pulse 39 between times K and L. Moreover, the time separating the longer pulse and the shorter pulse between times J and K is characterized by a non-zero varying voltage as is the voltage following the shorter pulse between time K and L. The overall effect is to excite the natural ringing or resonant frequency of the piezo transducer with the longer pulse 37 between times I and J and the higher harmonic with the shorter pulse between times K and L. Of course, as indicated previously, the shorter pulse may precede or follow the longer pulse using the wave forms of Fig. 4. Alternate pulses 37a and 37b are shown in Fig. 4a where the shorter pulse follows the longer pulse.

**[0028]** As indicated previously, the preferred embodiment, whether utilizing the wave form of Figs. 2A, 2A', 4 or 4A, provides for a longer pulse of 14.5 microseconds and a shorter pulse 3.0 microseconds. Other embodiments, depending upon the resonant frequency of the transducer, may incorporate other durations. For example, the pulse of the longer duration may be between

5 microseconds and 100 microseconds whereas the pulse of the shorter duration may be between .5 microseconds and 6 microseconds. Similarly, time between pulses may vary between .1 microsecond and 5 microseconds.

[0029] Referring again to Fig. 4, the waveform described therein is particularly desirable to achieve stable performance. In order to achieve the waveform of Fig. 4, it would be desirable to include a resistance in series with the piezoelectric transducer. In this regard, reference is made to Fig. 5 wherein a resistor 40 of at least 100 ohms is connected in series with a transducer 10 located between an electrode 42 and an electrode 44. As shown, the transducer 10 is a length mode transducer which achieves the transducer expansion and contraction shown in Figs. 2B and 2C and has a length less than .6 inches. The transducer 10 is coupled to the chamber 14 through a diaphragm 46. An inlet 48 leading into the chamber 14 is also shown. In the preferred embodiment, the chamber 14 would have a sufficiently small volume so as to assure a high Helmholtz resonant frequency in excess of 50 kHz and preferably approaching 90 kHz and would be embodied in the printhead shown in U.S. Patent Application Serial No. 08/828,758 filed March 25, 1997 which is incorporated by reference. Further details concerning the particular impulse ink jet disclosed in Fig. 5 may be found with reference to U.S. Patent No. 4,697,193 which is incorporated herein by reference although it will be understood that Helmholtz frequencies in excess of 50 kHz are not disclosed in the aforesaid patent.

[0030] As shown in Fig. 6, a voltage waveform similar to that shown in Fig. 4a is superimposed on the chamber pressure of the fluid jet device depicted in Figs. 2B and 2C. It will be noted that the chamber pressure variation corresponding to the resonant frequency of the device is basically sinusoidal and decaying as a result of the longer pulse 37b but carries a slight ripple as a result of the shorter pulse 39b which excites the higher harmonic of the device. The ripple which corresponds to the higher harmonic of the device takes the shape of a step 50 coinciding with the trailing edge 52 of the shorter pulse 39b actually causes the tail of the droplet to break off to create a smaller droplet as shown in Fig. 2C. As a result, the droplet is able to travel further at higher velocities; i.e., the throw distance is increased.

[0031] It will be appreciated that the higher harmonic frequency of the transducer must be excited in a way so as to assure that the tail of the droplet is accelerated into the droplet and not decelerated. In order to depict the proper relationship between the resonant frequency of the transducer and the higher harmonic frequency, reference is made to Fig. 6 wherein the resonant frequency is depicted by the generally sinusoidal wave shape 48 and the higher harmonic frequency is depicted by the sinusoidal waveform 50 properly phased by the timing of the pulses such that a specific high harmonic frequency is excited. This relationship between the high-

er harmonic and the resonant frequency will assure that the tail is broken off and the remainder of the tail which stays with the droplet will be accelerated into the droplet head thereby improving throw distance and velocity. Although particular transducers and particular voltage waveforms have been shown, it will be appreciated that this invention may be practiced with a variety of devices including bubble jets where the fluid or ink itself serves as a transducer. In addition, the invention may be practiced with other shapes and forms of transducers, i.e., not necessarily length mode expander transducers. For example, benders and shared wall transducers may be used. Moreover, the particular drive waveform may not be a voltage but any energy pulse so as to energize and deenergize the transducer at the appropriate times to assure the excitation of the resonant frequency as well as the higher harmonic frequency. Finally, the fluid need not be ink but may comprise any liquid which must be jetted in droplet form for any purpose, e.g. metering.

### Claims

1. A method of operating an impulse fluid jet device comprising a chamber (14) having an orifice (16) for ejection of droplets (20) in response to different energy pulses (23,25; 37, 39; 37a, 39a) applied to a transducer (10), said transducer (10) having a resonant frequency and a higher harmonic frequency, said method being characterized by the following steps:

generating one energy pulse (23; 37; 37a) for one duration coupled to the transducer (10) for exciting the resonant frequency of the transducer (10), thus

initiating the ejection of a droplet (20) having a head portion and an attached tail (22) portion in response to the one energy pulse (23), wherein the tail portion (22) is integral with the fluid at the orifice (16);

generating another energy pulse (25; 39; 39a) of another duration coupled to the transducer (10), said other duration being substantially shorter than said one duration for exciting the higher harmonic frequency of the transducer (10), wherein the higher harmonic frequency generates a pressure wave such that the tail portion (22) breaks from the fluid at the orifice (16) and the tail portion (22) and the head portion of the droplet (20) travel at substantially the same velocity toward a target (36).

2. The method of claim 1 wherein said device has a Helmholtz fluidic frequency in excess of 50 kHz.
3. The method of claim 1 or 2 wherein said resonant frequency is greater than 75 kHz and said higher

harmonic frequency is greater than 200 kHz.

4. The method of at least one of the preceding claims wherein said one duration is greater than 5  $\mu$ sec.

5. The method of at least one of the preceding claims wherein said other duration is greater than 0,5  $\mu$ sec.

6. The method of claim 1 wherein said one duration is between 5  $\mu$ sec and 100  $\mu$ sec and said other duration is between 0,5  $\mu$ sec and 6  $\mu$ sec.

7. The method of at least one of the preceding claims further comprising the step of waiting a period of time between generating the one (23; 37; 37a) and the other energy pulses (25; 39; 39a).

8. The method of claim 7 wherein a time delay between said one energy pulse (23; 37; 37a) and said other energy pulse (25; 39; 39a) is equal to at least 0,1  $\mu$ sec.

9. The method of claim 7 wherein a time delay between said one energy pulse (23; 37; 37a) and said other energy pulse (25; 39; 39a) is between 0,1  $\mu$ sec and 5  $\mu$ sec.

10. The method of at least one of the preceding claims wherein the resonant frequency to the transducer (10) is in excess of 50 kHz.

11. The method of at least one of the preceding claims wherein the higher harmonic frequency is in excess of 150 kHz.

12. An impulse fluid jet apparatus comprising:

a fluid jet chamber (14) having an orifice (16); a piezoelectric transducer (10) coupled to said jet chamber (14) so as to expand therein, said transducer having a resonant frequency and a higher harmonic frequency;

pulse generating circuitry (26) coupled to the transducer (10) for generating pulses (23, 25; 37, 39; 37a, 39a) for changing the state of energization of the transducer (10) for ejecting droplets (20) of fluid from the orifice (16) on demand, **characterized in that** said circuitry (26) generates one pulse (23; 37; 37a) having a first duration thus exciting said resonant frequency and initiating the ejection of a droplet (20) of fluid, said droplet (20) having a head portion and an attached tail portion (22), the droplet tail portion (22) being integral with the fluid at the orifice (16), and wherein said circuitry (26) generates another pulse (25; 39; 39a) having a duration substantially shorter than said one pulse (23; 37; 37a), thus exciting said higher harmon-

ic frequency of the transducer (10) and generating a pressure wave that breaks the tail portion (22) of the droplet (20) from said fluid at the orifice (16), such that the tail portion (22) and the head portion travel at substantially the same velocity toward a target (36).

13. The apparatus of claim 12 wherein the other pulse (25; 39; 39a) follows the one pulse (23; 37; 37a) in time.

14. The apparatus of claim 12 wherein the other pulse (25; 39; 39a) precedes the one pulse (23; 37; 37a) in time.

15. The apparatus of at least one of the claims 12 to 14 wherein said transducer (10) is of the length mode expander type.

16. The apparatus of at least one of the claims 12 to 15 wherein said resonant frequency of the transducer is greater than 50 kHz and said higher harmonic frequency is greater than 200 kHz.

17. The apparatus of at least one of the claims 12 to 16 wherein said one pulse (23; 37; 37a) has a duration greater than 5  $\mu$ sec.

18. The apparatus of at least one of the claims 12 to 17 wherein said other pulse (25; 39; 39a) has a duration greater than 0,5  $\mu$ sec.

19. The apparatus of at least one of the claims 12 to 18 wherein said pulse generating circuitry (26) generates said one pulse (23; 37; 37a) having a duration between 5  $\mu$ sec and 100  $\mu$ sec and said other pulse (25; 39; 39a) having a duration between 0,5  $\mu$ sec and 6  $\mu$ sec.

20. The apparatus of at least one of the claims 12 to 19 wherein said pulse generating circuitry (26) creates a delay between said one pulse (23; 37; 37a) and said other pulse (25; 39; 39a) in excess of 0,1  $\mu$ sec.

21. The apparatus of at least one of the claims 12 to 20 wherein said pulse generating circuitry generates a delay between said one pulse (23; 37; 37a) and said other pulse (25; 39; 39a) between 0,1  $\mu$ sec and 5  $\mu$ sec.

22. The apparatus of at least one of the claims 12 to 21 wherein said pulse generating circuitry includes a resistance (40) in series with said transducer (10) of at least 100 ohms, such that the waveform of the other pulse (25; 39; 39a) is sufficiently square to excite the higher harmonic frequency generating the pressure wave.

23. The apparatus of claim 22 wherein said resistance (40) is between 100 and 500 ohms.
24. The apparatus of at least one of the claims 12 to 23 wherein said higher harmonic frequency of the transducer (10) is in excess of 150 kHz.
25. The apparatus of at least one of the claims 12 to 24 wherein said resonant frequency of the transducer (10) is in excess of 50 kHz.

#### Patentansprüche

1. Verfahren zum Betreiben einer Impulsfluidstrahlvorrichtung enthaltend eine Kammer (14) mit einer Öffnung (16) zum Ausstoßen von Tröpfchen (20) als Antwort auf verschiedene Energieimpulse (23, 25; 37, 39; 37a, 39a), welche an einen Wandler (10) angelegt werden, wobei der Wandler (10) eine Resonanzfrequenz und eine höhere harmonische Frequenz hat, und das Verfahren **gekennzeichnet ist durch** die folgenden Schritte:
  - Erzeugen eines Energieimpulses (23; 37; 37a) für eine Dauer, gekuppelt mit dem Wandler (10), um die Resonanzfrequenz des Wandlers (10) zu erregen und so das Ausstoßen eines Tröpfchens (20) einzuleiten, welches einen Kopfabschnitt und einen anhängenden Schwanzabschnitt (22) hat als Antwort auf den einen Energieimpuls (23), wobei der Schwanzabschnitt (22) mit dem Fluid an der Öffnung (16) integral ist; Erzeugen eines anderen Energieimpulses (25; 39; 39a) mit einer anderen Dauer, gekuppelt mit dem Wandler (10), wobei die andere Dauer wesentlich kürzer ist als die eine Dauer, um die höhere harmonische Frequenz des Wandlers (10) zu erregen, wobei die höhere harmonische Frequenz eine Druckwelle erzeugt, so dass der Schwanzabschnitt (22) vom Fluid an der Öffnung (16) abbricht und der Schwanzabschnitt (22) und der Kopfabschnitt des Tröpfchens (20) mit im wesentlichen der gleichen Geschwindigkeit zu einem Ziel (36) hin fliegen.
2. Verfahren nach Anspruch 1, wobei die Vorrichtung eine Helmholtz-Fluidfrequenz von über 50 kHz hat.
3. Verfahren nach Anspruch 1 oder 2, wobei die Resonanzfrequenz größer ist als 75 kHz, und die höhere harmonische Frequenz größer ist als 200 kHz.
4. Verfahren nach mindestens einem der vorhergehenden Ansprüche, wobei die eine Dauer größer als 5 µs ist.
5. Verfahren nach mindestens einem der vorhergehenden Ansprüche, wobei die andere Dauer größer als 0,5 µs ist.
6. Verfahren nach Anspruch 1, wobei die eine Dauer zwischen 5 µs und 100 µs liegt und die andere Dauer zwischen 0,5 µs und 6 µs.
7. Verfahren nach mindestens einem der vorhergehenden Ansprüche, ferner enthaltend den Schritt des Wartens für einen Zeitraum zwischen dem Erzeugen des einen (23; 37; 37a) und des anderen Energieimpulses (25; 39; 39a).
8. Verfahren nach Anspruch 7, wobei eine Zeitverzögerung zwischen dem einen Energieimpuls (23; 37; 37a) und dem anderen Energieimpuls (25; 39; 39a) mindestens 0,1 µs beträgt.
9. Verfahren nach Anspruch 7, wobei eine Zeitverzögerung zwischen dem einen Energieimpuls (23; 37; 37a) und dem anderen Energieimpuls (25; 39; 39a) zwischen 0,1 µs und 5 µs liegt.
10. Verfahren nach mindestens einem der vorhergehenden Ansprüche, wobei die Resonanzfrequenz zum Wandler (10) über 50 kHz liegt.
11. Verfahren nach mindestens einem der vorhergehenden Ansprüche, wobei die höhere harmonische Frequenz über 150 kHz liegt.
12. Impulsfluidstrahlgerät enthaltend:
  - eine Fluidstrahlkammer (14) mit einer Öffnung (16);
  - einen piezoelektrischen Wandler (10), welcher mit der Strahlkammer (14) gekuppelt ist, um darin zu expandieren, wobei der Wandler eine Resonanzfrequenz hat und eine höhere harmonische Frequenz; wobei der Impuls erzeugende Schaltkreis (26) an den Wandler (10) gekuppelt ist, um Impulse (23, 25; 37, 39; 37a, 39a) zu erzeugen zur Änderung des Zustandes der Energiezufuhr zum Wandler (10) zum Ausstoßen von Tröpfchen (20) des Fluids aus der Öffnung (16) nach Bedarf, **dadurch gekennzeichnet**, dass der Schaltkreis (26) einen Impuls (23; 37; 37a) erzeugt, welcher eine erste Dauer hat und so die Resonanzfrequenz erregt und das Ausstoßen eines Fluidtröpfchens (20) einleitet, wobei das Tröpfchen (20) einen Kopfabschnitt und einen anhängenden Schwanzabschnitt (22) aufweist, der Tröpfchen-Schwanzabschnitt (22) mit dem Fluid an der Öffnung (16) integral ist, und der Schaltkreis (26) einen anderen Impuls (25; 39; 39a) erzeugt, welcher eine wesentlich kürzere Dauer hat als der eine

- Impuls (23; 37; 37a) und so die höhere harmonische Frequenz des Wandlers (10) erregt und eine Druckwelle erzeugt, welche den Schwanzabschnitt (22) des Tröpfchens (20) des Fluids an der Öffnung (16) abbricht, so dass der Schwanzabschnitt (22) und der Kopfabschnitt mit im wesentlichen der gleichen Geschwindigkeit zu einem Ziel (36) fliegen.
13. Gerät nach Anspruch 12, wobei der andere Impuls (25; 39; 39a) dem einen Impuls (23; 37; 37a) zeitlich folgt. 10
14. Gerät nach Anspruch 12, wobei der andere Impuls (25; 39; 39a) dem einen Impuls (23; 37; 37a) zeitlich vorausgeht. 15
15. Gerät nach mindestens einem der Ansprüche 12 bis 14, wobei der Wandler (10) vom Längsmodus-Expandertyp ist. 20
16. Gerät nach mindestens einem der Ansprüche 12 bis 15, wobei die Resonanzfrequenz des Wandlers größer ist als 50 kHz und die höhere harmonische Frequenz größer ist als 200 kHz. 25
17. Gerät nach mindestens einem der Ansprüche 12 bis 16, wobei der eine Impuls (23; 37; 37a) eine Dauer von mehr als 5  $\mu$ s hat. 30
18. Gerät nach einem der Ansprüche 12 bis 17, wobei der andere Impuls (25; 39; 39a) eine Dauer von mehr 0,5  $\mu$ s hat. 35
19. Gerät nach mindestens einem der Ansprüche 12 bis 18, wobei der Impuls erzeugende Schaltkreis (26) den einen Impuls (23; 37; 37a) erzeugt, welcher eine Dauer zwischen 5  $\mu$ s und 100  $\mu$ s hat, und den anderen Impuls (25; 39; 39a), welcher eine Dauer zwischen 0,5  $\mu$ s und 6  $\mu$ s hat. 40
20. Gerät nach mindestens einem der Ansprüche 12 bis 19, wobei der Impuls erzeugende Schaltkreis (26) eine Verzögerung zwischen dem einen Impuls (23; 37; 37a) und dem anderen Impuls (25; 39; 39a) von über 0,1  $\mu$ s erzeugt. 45
21. Gerät nach mindestens einem der Ansprüche 12 bis 20, wobei der Impuls erzeugende Schaltkreis eine Verzögerung zwischen dem einen Impuls (23; 37; 37a) und dem anderen Impuls (25; 39; 39a) zwischen 0,1  $\mu$ s und 5  $\mu$ s erzeugt. 50
22. Gerät nach mindestens einem der Ansprüche 12 bis 21, wobei der Impuls erzeugende Schaltkreis einen Widerstand (40) in Reihe mit dem Wandler (10) von mindestens 100 Ohm aufweist, so dass die Wellenform des anderen Impulses (25; 39; 39a) ausrei-

chend rechteckig ist, um die höhere harmonische Frequenz zu erregen, welche die Druckwelle erzeugt.

23. Gerät nach Anspruch 22, wobei der Widerstand (40) zwischen 100 und 500 Ohm liegt. 5
24. Gerät nach mindestens einem der Ansprüche 12 bis 23, wobei die höhere harmonische Frequenz des Wandlers über 150 kHz liegt. 10
25. Gerät nach mindestens einem der Ansprüche 12 bis 24, wobei die Resonanzfrequenz des Wandlers über 50 kHz liegt. 15

#### Revendications

1. Procédé d'exploitation d'un dispositif à jet de fluide par impulsions comprenant une chambre (14) ayant un orifice (16) pour l'éjection de gouttelettes (20) en réponse à différentes impulsions d'énergie (23, 25; 37, 39; 37a, 39a) appliquées à un transducteur (10), ledit transducteur (10) ayant une fréquence de résonance et une fréquence harmonique supérieure, ledit procédé étant **caractérisé** par les étapes consistant à:
  - générer une première impulsion d'énergie (23; 37; 37a) pendant une première durée appliquée au transducteur (10) en vue d'exciter la fréquence de résonance du transducteur (10), et ainsi déclencher l'éjection d'une gouttelette (20) ayant une partie tête et une partie queue attachée (22) en réponse à la première impulsion d'énergie (23), la partie queue (22) étant d'un seul tenant avec le fluide au niveau de l'orifice (16);
  - générer une autre impulsion d'énergie (25; 39; 39a) d'une autre durée appliquée au transducteur (10), ladite autre durée étant sensiblement plus courte que ladite première durée en vue d'exciter la fréquence harmonique supérieure du transducteur (10), ladite fréquence harmonique supérieure générant une onde de pression telle que la partie queue (22) se sépare du fluide au niveau de l'orifice (16) et la partie queue (22) et la partie tête de la gouttelette (20) se déplacent sensiblement à la même vitesse vers une cible (36).
2. Procédé selon la revendication 1, dans lequel ledit dispositif a une fréquence fluide de Helmholtz supérieure à 50 kHz.
3. Procédé selon la revendication 1 ou 2, dans lequel ladite fréquence de résonance est supérieure à 75



- kHz et ladite fréquence harmonique supérieure est supérieure à 200 kHz.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite première durée est supérieure à 5  $\mu$ s. 5
  5. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite autre durée est supérieure à 0,5  $\mu$ s. 10
  6. Procédé selon la revendication 1, dans lequel ladite première durée est comprise entre 5  $\mu$ s et 100  $\mu$ s et ladite autre durée est comprise entre 0,5  $\mu$ s et 6  $\mu$ s. 15
  7. Procédé selon l'une quelconque des revendications précédentes, comprenant en outre l'étape consistant à attendre un laps de temps entre la génération de la première (23; 37; 37a) et de l'autre impulsion d'énergie (25; 39; 39a). 20
  8. Procédé selon la revendication 7, dans lequel un retard temporel entre ladite première impulsion d'énergie (23; 37; 37a) et ladite autre impulsion d'énergie (25; 39; 39a) est égal à au moins 0,1  $\mu$ s. 25
  9. Procédé selon la revendication 7, dans lequel un retard temporel entre ladite première impulsion d'énergie (23; 37; 37a) et ladite autre impulsion d'énergie (25; 39; 39a) est compris entre 0,1  $\mu$ s et 5  $\mu$ s. 30
  10. Procédé selon l'une quelconque des revendications précédentes, dans lequel la fréquence de résonance du transducteur (10) est supérieure à 50 kHz. 35
  11. Procédé selon l'une quelconque des revendications précédentes, dans lequel la fréquence harmonique supérieure est supérieure à 150 kHz. 40
  12. Dispositif à jet de fluide par impulsions, comprenant:
    - une chambre d'émission de jet de fluide (14) 45 ayant un orifice (16);
    - un transducteur piézoélectrique (10) couplé à ladite chambre d'émission de jet (14) de manière à s'allonger en son sein, ledit transducteur ayant une fréquence de résonance et une fréquence harmonique supérieure; 50
    - un circuit générateur d'impulsions (26) couplé audit transducteur (10) pour générer des impulsions (23, 25; 37, 39; 37a, 39a) en vue de changer l'état d'excitation du transducteur (10) pour éjecter des gouttelettes (20) de fluide par l'orifice (16) à la demande, **caractérisé en ce que** ledit circuit (26) génère une première impulsion 55
- (23; 37; 37a) ayant une première durée pour ainsi exciter ladite fréquence de résonance et déclencher l'éjection d'une gouttelette (20) de fluide, ladite gouttelette (20) ayant une partie tête et une partie queue attachée (22), la partie queue (22) de la gouttelette étant d'un seul tenant avec le fluide au niveau de l'orifice (16), et **en ce que** ledit circuit (26) génère une autre impulsion (25; 39; 39a) ayant une durée sensiblement plus courte que ladite première impulsion (23; 37; 37a), pour ainsi exciter ladite fréquence harmonique supérieure du transducteur (10) et générer une onde de pression qui sépare la partie queue (22) de la gouttelette (20) dudit fluide au niveau de l'orifice (16), de sorte que la partie queue (22) et la partie tête se déplacent sensiblement à la même vitesse vers une cible (36).
13. Dispositif selon la revendication 12, dans lequel l'autre impulsion (25; 39; 39a) suit la première impulsion (23; 37; 37a) dans le temps.
  14. Dispositif selon la revendication 12, dans lequel l'autre impulsion (25; 39; 39a) précède la première impulsion (23; 37; 37a) dans le temps.
  15. Dispositif selon l'une quelconque des revendications 12 à 14, dans lequel ledit transducteur (10) est du type à déformation en mode longitudinal.
  16. Dispositif selon l'une quelconque des revendications 12 à 15, dans lequel ladite fréquence de résonance du transducteur est supérieure à 50 kHz et ladite fréquence harmonique supérieure est supérieure à 200 kHz.
  17. Dispositif selon l'une quelconque des revendications 12 à 16, dans lequel ladite première impulsion (23; 37; 37a) a une durée supérieure à 5  $\mu$ s.
  18. Dispositif selon l'une quelconque des revendications 12 à 17, dans lequel ladite autre impulsion (25; 39; 39a) a une durée supérieure à 0,5  $\mu$ s.
  19. Dispositif selon l'une quelconque des revendications 12 à 18, dans lequel ledit circuit générateur d'impulsions (26) génère ladite première impulsion (23; 37; 37a) ayant une durée comprise entre 5  $\mu$ s et 100  $\mu$ s et ladite autre impulsion (25; 39; 39a) ayant une durée comprise entre 0,5  $\mu$ s et 6  $\mu$ s.
  20. Dispositif selon l'une quelconque des revendications 12 à 19, dans lequel ledit circuit générateur d'impulsions (26) crée un retard entre ladite première impulsion (23; 37; 37a) et ladite autre impulsion (25; 39; 39a) supérieur à 0,1  $\mu$ s.

21. Dispositif selon l'une quelconque des revendications 12 à 20, dans lequel ledit circuit générateur d'impulsions (26) génère un retard entre ladite première impulsion (23; 37; 37a) et ladite autre impulsion (25; 39; 39a) compris entre 0,1  $\mu$ s et 5  $\mu$ s. 5
22. Dispositif selon l'une quelconque des revendications 12 à 21, dans lequel ledit circuit générateur d'impulsions (26) comprend une résistance (40) en série avec ledit transducteur (10) d'au moins 100 ohms, de sorte que la forme d'onde de l'autre impulsion (25; 39; 39a) est suffisamment carrée pour exciter la fréquence harmonique supérieure générant l'onde de pression. 10 15
23. Dispositif selon la revendication 22, dans lequel ladite résistance (40) est comprise entre 100 et 500 ohms.
24. Dispositif selon l'une quelconque des revendications 12 à 23, dans lequel ladite fréquence harmonique supérieure du transducteur (10) est supérieure à 150 kHz. 20
25. Dispositif selon l'une quelconque des revendications 12 à 24, dans lequel ladite fréquence de résonance du transducteur (10) est supérieure à 50 kHz. 25

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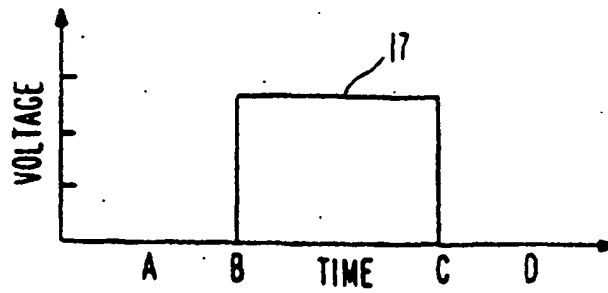
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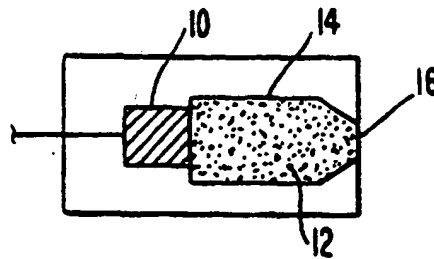
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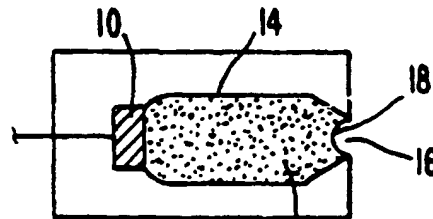
PRIOR ART  
***Fig. 1A***



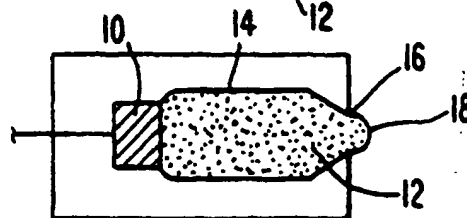
PRIOR ART  
***Fig. 1B***



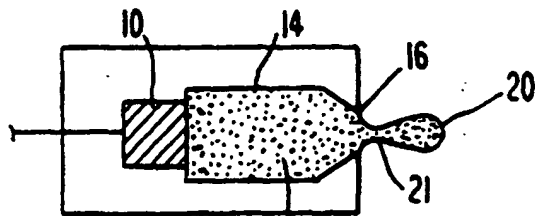
PRIOR ART  
***Fig. 1C***



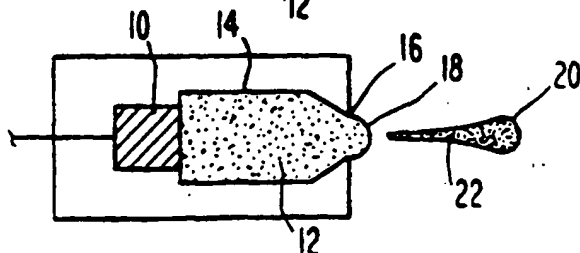
PRIOR ART  
***Fig. 1D***



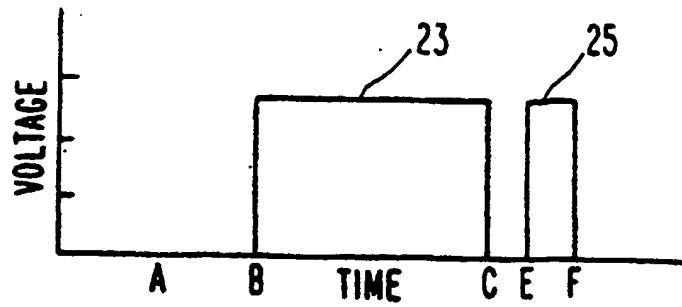
PRIOR ART  
***Fig. 1E***



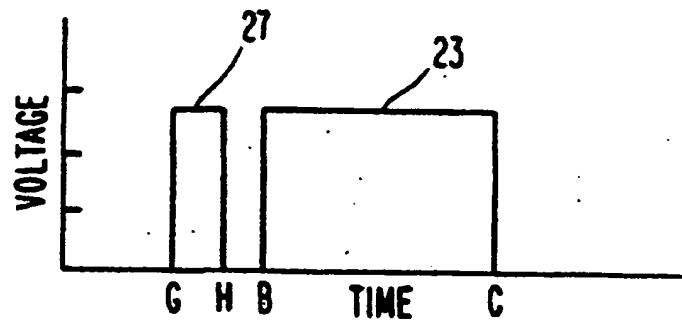
PRIOR ART  
***Fig. 1F***



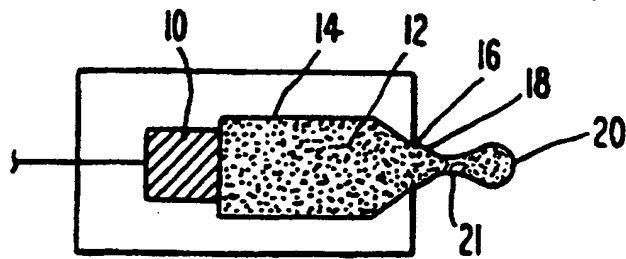
***Fig. 2A***



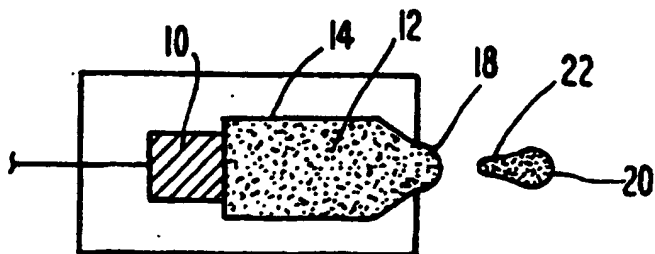
***Fig. 2A'***

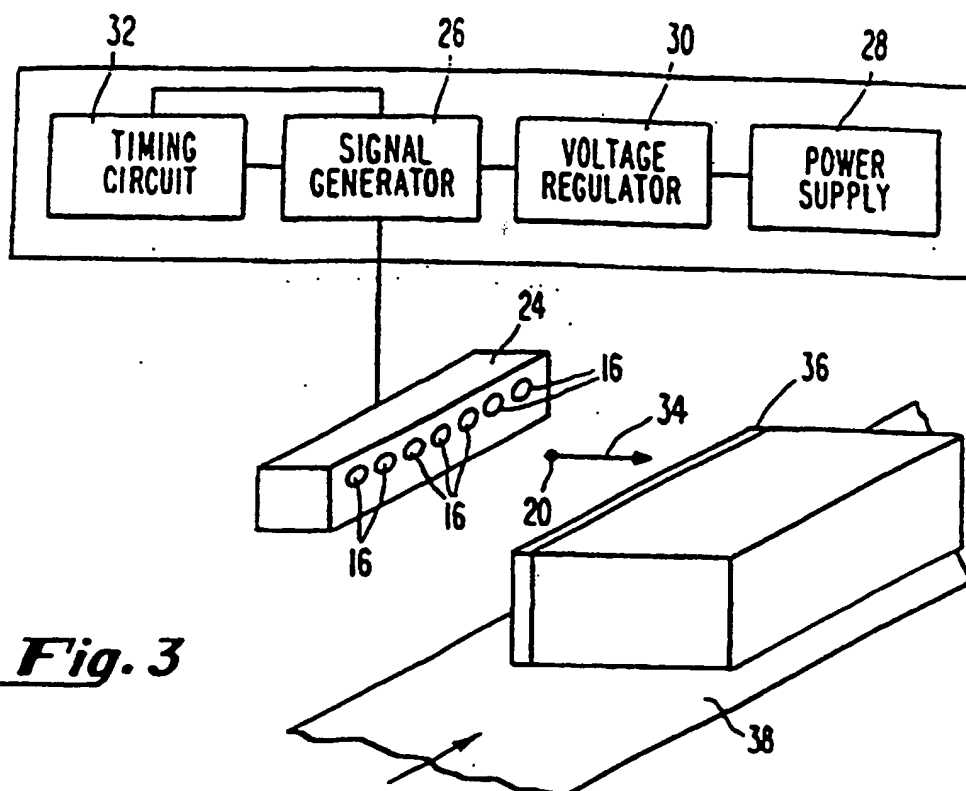


***Fig. 2B***

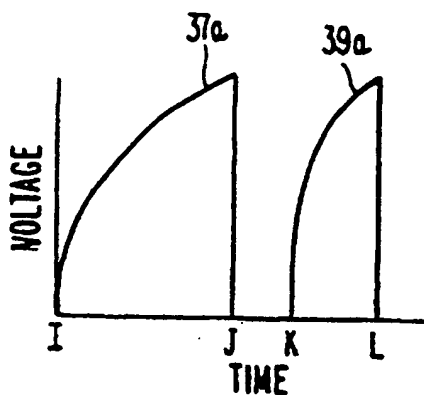


***Fig. 2C***

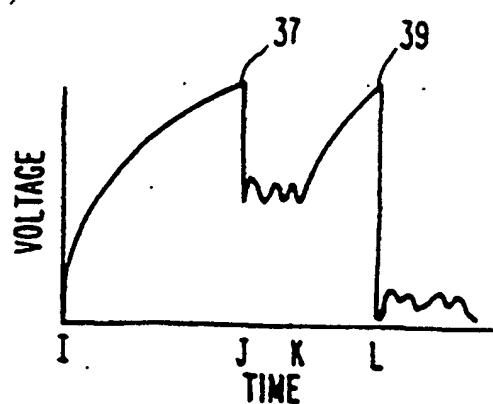




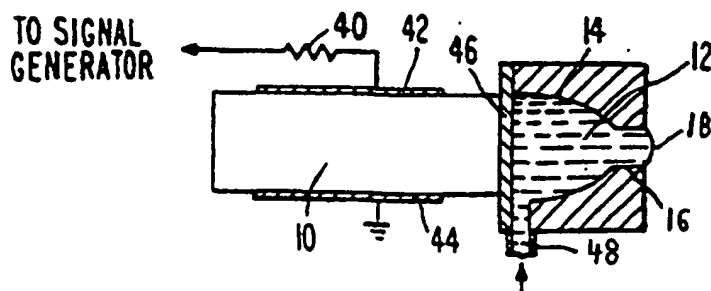
**Fig. 3**



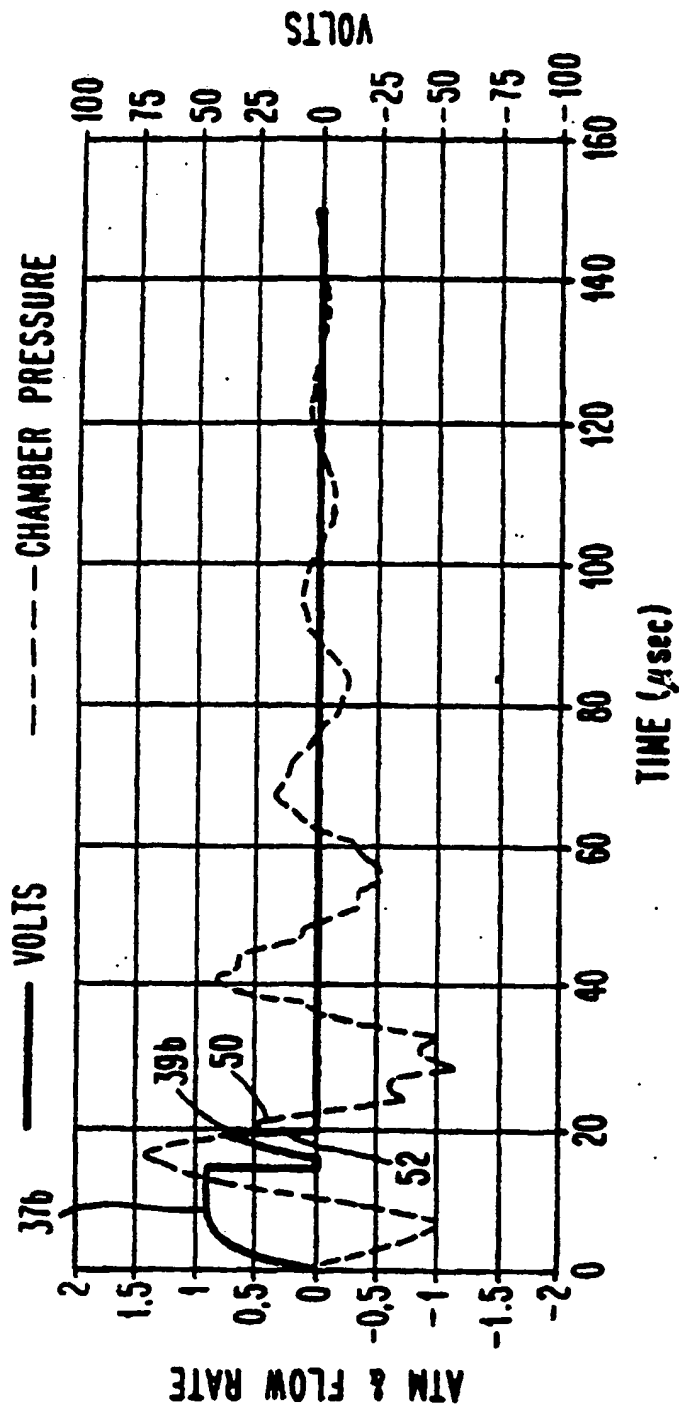
**Fig. 4a**



**Fig. 4**



**Fig. 5**



**Fig. 6**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant: Lui et al.  
Serial No.: Applied for Herewith (Divisional of 09/949,973)  
Filed: Herewith  
For: HIGH THREONINE PRODUCING LINES OF *NICOTIANA*  
*TOBACUM* AND METHODS FOR PRODUCING  
Examiner: Unassigned  
Art Unit: Unassigned

Assistant Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

Please amend the above-cited application as indicated. Applicant respectfully requests entry of the amendment for purposes of determining the filing fee. If extra fees are due, the Commissioner is hereby authorized to charge any fees due to Deposit Account No. 16-1435. A duplicate this sheet is enclosed for that purpose.

**PRELIMINARY AMENDMENT**

**In The Specification**

On page 6, immediately after the heading "Brief Description of the Drawings" please insert the following sentence as the first paragraph:

The file of this patent contains at least one drawing executed in color. Copies of this patent with color drawing(s) will be provided by the Patent and Trademark Office upon request and payment of the necessary fee.

On page 35 please replace the second full paragraph starting "A deposit of seeds" with the following:

A deposit of seeds from a modified line of *N. tabacum* made by the methods of the invention (strain 120B derived from parent line K-326 and described in Table 2) was made on August 29, 2001, to the American Type Culture Collection (ATCC, 10801 University Blvd., Manassas, VA 20110-2209), under conditions prescribed by the Budapest Treaty. The ATCC accession number for the deposited strain is PTA-3673.

**In The Claims**

Please cancel claims 1-10 and 48-52.



REMARKS

This application is a divisional application of U.S. Application Serial No. 09/1949,973. Upon entry of the foregoing amendment, claims 35-55 are pending, with claims 1-34 canceled.

The changes made by this amendment are shown on the attached sheet as required under 37 CFR 1.121.

Regarding the addition of a description of color photographs, Applicant herewith submits three copies of color photographs and a petition under 37.C.F.R. 1.84 requesting that color photographs be substituted for Figures 3-7 as submitted with the Application as filed herewith.

The amendment also identifies the ATCC accession number for a deposit for *N. tabacum* strain 120B that is described in the specification. The deposit was received by ATCC on August 29, 2001, and the seeds found to be viable as required under 37 CFR 1.807 (See Appendix A, attached herein). Applicant notes that under 37 C.F.R. § 1.802(c), providing this information does not admit that a deposit is required under 35 USC § 112.

**Version With Markings to Show Changes Made Pursuant to 37 CFR 1.121**

In accordance with 37 CFR 1.121, the following version of the specification and claims as rewritten by the foregoing amendment show all the changes made relative to the previous versions of the claims, with additions underlined and deletions [bracketed]. For clarity, the canceled claims not shown but delineated as canceled.

**In The Specification**

**Page 6, Immediately after the heading “Brief Description of the Drawings”:**

Please insert the following sentence as the first paragraph:

The file of this patent contains at least one drawing executed in color. Copies of this patent with color drawing(s) will be provided by the Patent and Trademark Office upon request and payment of the necessary fee.

**On page 35 Second full paragraph:**

A deposit of seeds from a modified line of *N. tabacum* made by the methods of the invention (strain 120B derived from parent line K-326 and described in Table 2) was made on August 29, 2001, to the American Type Culture Collection (ATCC, 10801 University Blvd., Manassas, VA 20110-2209), under conditions prescribed by the Budapest Treaty[]. The ATCC accession number for the deposited strain is [ ] PTA-3673.

**In The Claims**

Please cancel claims 1-10 and 48-52.

**CONCLUSION**

In view of the foregoing amendment and remarks, each of the claims now pending in the application is in immediate condition for allowance. The Examiner is respectfully invited to telephone the undersigned at (336) 747-7541 to discuss any questions relating to the application.

Respectfully submitted,

Date: \_\_\_\_\_

\_\_\_\_\_  
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**[BE/BE]; Allée de la Recherche 60, B-1070 Brussels (BE).**
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- (74) Agent: **KIRK, Martin**; Allée de la Recherche 60, B-1070 Brussels (BE).
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— *without international search report and to be republished upon receipt of that report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



**WO 02/08309 A2**

(54) Title: **USE OF CROSS-LINKER AND COMPOSITIONS MADE THEREFROM**

(57) Abstract: The invention provides a method of polymerizing or crosslinking cationically curable components using X-rays, gamma rays or electron beam as an energy source. As the initiator for the cationic polymerization, an onium gallate compound having an anion of the formula  $GaX_nR_b$  wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4 is disclosed. The invention also provides a composite material and a method for preparing the composite material using an electron beam and the onium gallate compound as an initiator. Finally, disclosed is a photoresist material containing the onium gallate compound as the acid generator or crosslinking initiator.

### USE OF CROSS-LINKER AND COMPOSITIONS MADE THEREFROM

The present invention relates use of a cross-linker and compositions made therefrom, in particular to use of an onium gallate initiator for polymerization and/or crosslinking of cationic active components via an electron beam, in composite and photoresist compositions.

Cationically curable systems which contain components that polymerize or crosslink in the presence of strong acids have been developed and improved over the last 15-20 years. Recent developments employ onium salts as initiators in these systems. These onium salts initiators generate strong acids upon exposure to an energy source, such as heat or electromagnetic radiation, e.g. actinic radiation, electron beam radiation, X-rays, gamma radiation, etc. The strong acids formed then cause the polymerization or crosslinking of cationically curable systems.

Electron beams (EB) have been used to polymerize and/or crosslink cationically curable components, among other uses. The electron beam uses high energy electrons from an accelerator to activate the decomposition of the onium salt initiator to form a strong acid, which initiates the polymerization and/or crosslinking of the cationically curable moieties.

Cationically polymerizable and/or crosslinkable systems have been used in fiber reinforced composites. Recently, attention has been given to using electron beams to crosslink resin matrices of composite materials. Using electron beams as the energy source for crosslinking the resin matrices of the composite material has advantages over thermal curing of the matrices. These advantages include, lower curing temperature, reduced curing times and improved handling, which result in improved product quality (improved physical properties) and lower production cost.

In addition, onium salt type initiators have been used as acid generators and crosslinking initiators for photoresist compositions used to form photo images and relief images. In forming such images, a composition containing a resin material is either crosslinked in the presence of an acid (so-called negative resist) or are degraded in the presence of an acid (so-called positive resist). Some onium salt type initiators are known to generate acids upon exposure to an energy source such as heat and photo-energy, e.g. UV radiation, electron beams, gamma

radiation, etc. In both types of photoresist systems, a resin component must be present in the photoresist composition which contains moieties that render the resin soluble in an aqueous alkaline solution. The aqueous alkaline solution is used to develop the resist material, thereby forming the image.

5

Based on investigations carried out by the inventors of the present application, a new class of onium salt initiators has been discovered and these onium salts are effective for the cationic polymerization or crosslinking of an acid curable component. It has further been discovered that the onium salts used in the present invention are also effective as curing initiators and acid generators for negative and positive photoresist compositions, respectively.

10

The onium salt initiator used in the methods and compositions of the present invention contains conventional onium salt cations. The new feature of the onium salts used in the methods and compositions of the present invention is the anion of the salt. The anion has the formula  $GaX_aR_b^-$ , wherein X is a halogen atom or a hydroxy group, R is an aryl group or substituted aryl group, a and b are each represent an integer of 0 to 4, provided that the sum of a and b is 4. The onium salt initiator of the present invention is referred to as an "onium gallate".

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20

DE 4024661 (Wewers et al) describes salts which are useful as initiators for polymerization of epoxy or vinyl groups. Optionally certain anions of these salts comprise gallium amongst many other possible elements. However these anions all comprise aliphatic " $-CF_3SO_3^-$ " groups and an anionic group such as  $Cl^-$  or  $SO_3^-$  to bear the negative charge.

25

EP 0442635 (=US 5084586 & US 5124417) (3M) also describe various salts which are useful as initiators for cationic polymerization and may comprise anions containing a gallium atom (again as an option from many other elements). However in these anions the gallium atom is always substituted directly with a " $-SO_3^-$ " group.

30

Thus the above prior art anions have a very different structure to those gallate anions described herein and used in the present invention. The onium gallates used in the methods and compositions of the present invention are described in the co-pending application WO 01/12720 (= US 6,166,233) of priority date August 17, 1999, which is hereby incorporated by reference.

35

- The first aspect of the present invention relates to a method of using actinic radiation, an electron beam (EB), X-Ray and/or gamma radiation to polymerize or crosslink a cationic polymerizable or crosslinkable component(s). It has been discovered that a composition containing a component which is capable of cationic polymerizing or cationic crosslinking and an onium salt having the anion described above can very effectively be polymerized or crosslinked using actinic radiation, X-rays, gamma rays and/or an electron beam to give compositions having improved properties. An electron beam is preferred.
- 10 A second aspect of the present invention is a composite formed by curing a cationically curable resin using the process of the first aspect. The composites contain reinforcing materials, such as fibers, in addition to the cationic active component and onium gallate initiator.
- 15 A third aspect of the present invention provides a photoresist material and a method for forming a photoresist relief image. In this aspect of the present invention, conventional resin materials used in photoresist materials, both negative and positive, are blended with the onium gallate. Further, the present invention also provided for a method of forming a photoresist relief image on a substrate by exposing the photo resist material to an energy source, followed by developing the exposed composition.

Other aspects of the present invention are given in the claims.

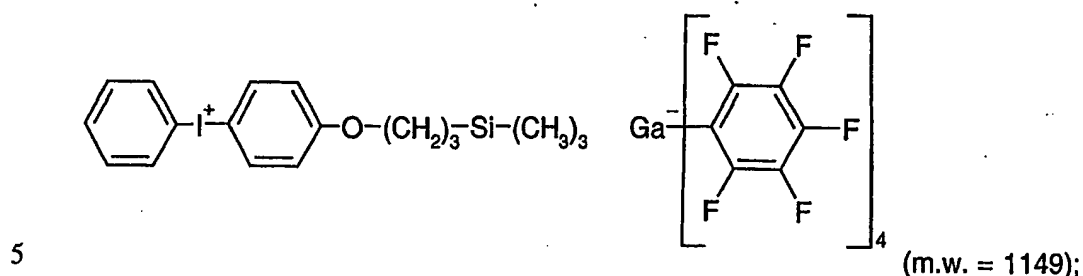
- 25 Therefore broadly in accordance with the present invention there is provided; a process for polymerizing or cross-linking a cationic polymerizable or cross-linkable component, said process comprising:
- a) forming a composition containing a component which is capable of cationic polymerizing or cationic cross-linking and an onium salt having an anion of the formula  $GaX_aR_b$  wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4; and
- 30 b) exposing the composition to radiation selected from the group consisting of actinic radiation, X-rays, gamma-rays and and/or an electron beam.

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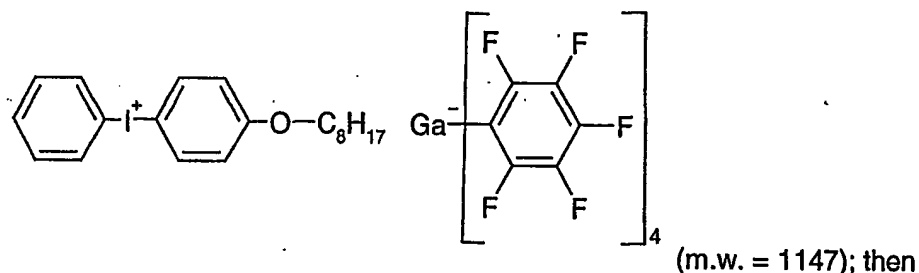
In the process of the present invention a preferred proviso is when:

4

the polymerizable component is a matrix of the diglycidyl ether of bisphenol-A available commercially from Dow Chemical under the trademark DER 332; and the onium salt is present in an amount of 1% by weight of the composition and is either:



or



the radiation used in step (b) is other than an electron beam at a beam voltage of 200mV and a dose of 10 Mrad.

10

Preferably the composition obtained and/or obtainable by the process of the invention has at least one of the following properties:

- i) a flexural modulus of less than about 2.5 Gpa, more preferably from about 2.0 to about 2.5 Gpa;
- 15 ii) a service temperature of greater than about 150°C, more preferably from about 150°C to about 160°C;
- iii) a  $T_g$  (measured in a conventional manner as a function of the loss modulus) of greater than about 180°C, more preferably from about 180°C to about 195°C; and/or
- 20 iv) a  $T_g$  (measured in a conventional manner as a function of the peak in a tan delta plot) of greater than about 207°C, more preferably from about 207°C to about 212°C.

25 The onium gallates used in the methods and compositions of the present invention are preferably those described in WO 01/12720. These onium gallates include a



cationic moiety and an anionic gallate moiety. The cationic moiety can be any cation of onium salts such as diaryl iodonium, iodonium, pyrylium, thiapyrylium, sulfonium, phosphonium, ferrocenium or diazonium ions. The preferred cation ions are diaryl iodonium cations or triaryl sulfonium cations.

5

The anionic gallate has the general formula  $GaX_aR_b^-$ , wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b each represent an integer of 0 to 4, provided that the sum of a and b is 4. The aryl groups representing R can be the same or different and may be aryl groups having an electron withdrawing capacity. Examples of such aryl groups include, but are not limited to, phenyl groups, phenyl groups substituted by at least one electron-withdrawing group, such as halogen atoms,  $CF_3$ ,  $NO_2$ , CN and the like; or is an aryl radical containing at least two aromatic ring members, such as biphenyl, naphthyl and the like, which are optionally substituted by electron withdrawing groups such as halogen atoms,  $CF_3$ ,  $NO_2$ , CN and the like. Preferably, the aryl groups are substituted with the electron withdrawing groups defined above. The preferred electron withdrawing groups are halogen atoms, most preferably, fluorine atoms.

The gallate anions which can be used in the methods and compositions of the present invention include, but are not limited to,  $[Ga(C_6F_5)_4]^-$ ,  $[Ga(C_6H_4CF_3)_4]^-$ ,  $[(C_6F_5)_2GaF_2]^-$ ,  $[(C_6F_5)GaF_3]^-$ , and  $[Ga(C_6H_3F_2)_4]^-$ .

Representative onium cations are well known to those skilled in the art and are described in detail in, for example, U.S. Patents 5,550,265, and 5,340,898 to Rhone-Poulenc Chimie and U.S. Patent 5,639,802 to Spectra Group Limited and include iodonium, pyrylium, thiapyrylium, sulphonium, phosphonium, ferrocenium, and diazonium ions. Preferred cations are, for example, aryl-iodonium ions such as 4-octyloxyphenylphenyl iodonium (OPPI), 4,4'-dimethyldiphenyliodonium, 4-(3-trimethylsilylpropyloxy)phenylphenyl iodonium and diphenyliodonium: sulphonium ions include triarylsulphonium ions such as triphenyl sulphonium ion and 4-octyloxyphenyl sulphonium ion. Particularly preferred is the cation OPPI, which tends to be more soluble in epoxy resins than other cations. However, other onium cations are known to those skilled in the art and can be used in the process and compositions of this invention.

35

The onium salts used in the methods and compositions of the present invention can be prepared by known methods, such as an exchange reaction between a salt of the cationic moiety and an alkali metal salt of the anionic moiety. Examples of

salts of the cationic moiety include, but are not limited to, halides such as chloride, iodide, etc. and other salts such as hexafluorophosphate, tetrafluoroborate, tosylate and others. Alkali metal salts and alkaline earth metal salts of the anionic moiety include salts such as sodium, lithium, potassium and magnesium salts.

- 5 The reaction conditions, including the respective amounts of the reactants, particular solvents, temperature and other reaction parameters can be easily determined by those skilled in the art. The methods used must permit recovery of the desired initiator salt in the solid state, by filtration of a precipitate formed or in an oily state by extraction using a suitable solvent.

10

The salts of the anionic moiety can be prepared by methods known to those skilled in the art. An example of a method which can be used is an exchange reaction between a halogallate compound and an organometallic compound. The metal atom in the organometallic compound can be, for example, magnesium, lithium, tin, cadmium, copper, zinc and other metals. The organic part of organometallic

15

compound should contain the desired organic groups in a stoichiometric amount. Optionally, the product of the exchange reaction can be further treated in a hydrolysis reaction using an aqueous solution of an alkali metal halide. The synthesis described above is analogous to the synthesis described in J. Organometallic Chemistry, vol. 178, p. 1-4, (1979); J.A.S.C., 82, 5298 (1960); Anal. Chem. Acta, 44, 175-183 (1969); U.S. Patent No. 4,139,681, hereby incorporated by reference, and Zh. Org. Khim., vol 25, No 5, pages 1099-1102, (May 1989).

20

- 25 Onium salts used to prepare the onium gallates used in the process and compositions of the present invention can be prepared by methods well known to those skilled in the art, including those methods described in U.S. Patents 5,550,265, 5,340,898, and 5,639,802, each hereby incorporated by reference.

30

In the method of the first aspect of the present invention, any component which can be polymerized or crosslinked via a cationic polymerization or crosslinking can be used. Examples of the components which can be polymerized or crosslinked via cationic polymerization or crosslinking are monomers, oligomers and polymers having one or more cationically curable functional groups. Examples of cationically

35

curable functional groups include, but are not limited to, epoxy groups, vinyl or allyl groups, vinyl ether groups, allyl ether groups, styrenic groups and styryloxy groups, cyclic ether containing groups including oxetane groups and others, cyclic ester containing groups, cyclic sulfide groups, melamine formaldehyde containing

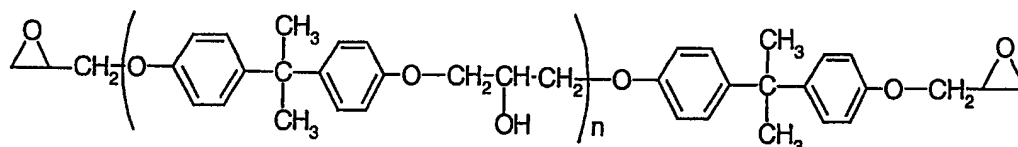
groups, phenolic formaldehyde groups, cyclic organosiloxane containing groups, lactone containing groups, lactam containing groups, and cyclic acetal containing groups.

- 5 The composition may also include additives, including reactive and non-reactive diluents, polyols, phenolic materials, toughening agents, and fillers such as silica, alumina, and titanium containing materials.

10 Particularly preferred cationic polymerizable or crosslinkable components used in the present invention are epoxy containing monomers, oligomers and polymers; vinyl ether containing monomers, oligomers, and polymers; and cyclic ether containing monomer, oligomers and polymers.

15 In particular, the epoxy resin can include those from any of the following glycidyl ethers:

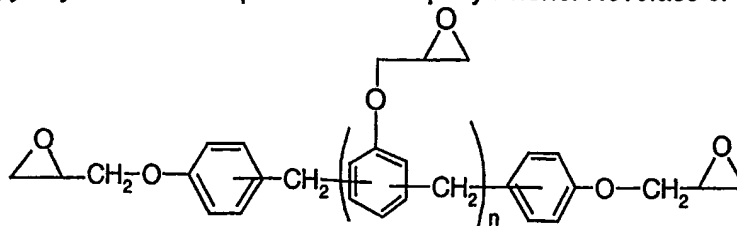
1 Diglycidyl ethers of Bisphenol A of the formula:



where  $n=0$  to 10.

20 These resins are available from a number of manufacturers such as Shell Chemical Company, DOW Chemical Company, and Ciba Specialty Chemicals Corporation in a variety of molecular weights and viscosities. Examples include: DER 332, DER 330, DER 331, DER. 383 (DOW trademarks); Epon 825, Epon 826, and Epon 828 (Shell trademarks); and Tactix 123, Tactix 138, and Tactix 177, 25 Araldite GY 6008, Araldite GY 6010, and Araldite GY 2600 (Ciba Specialty Chemicals Corporation trademarks).

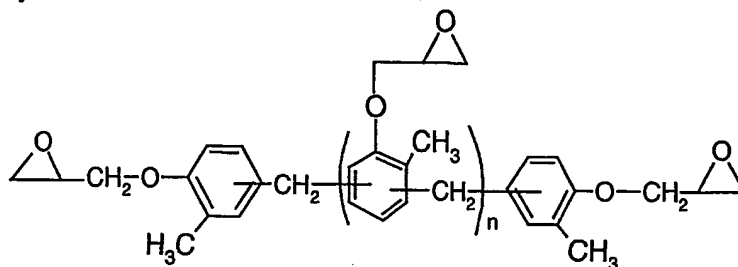
2A Diglycidyl ethers of Bisphenol F and Epoxy Phenol Novolacs of the formula:



Diglycidyl ethers of Bisphenol F, when  $n=0$ , or Epoxy Phenol Novolacs, when  $n>0$ .

These materials are available from a number of different manufacturers in a variety of molecular weights and viscosities. Examples include: Epon 155, Epon 160, Epon 861 and Epon 862 (Shell trademarks), DEN 431, DEN 436, DEN 438, 5 DEN 439, DEN 444, and Tactix 785 (Dow trademarks), Araldite PY 306, Araldite EPN 1138, Araldite EPN 1139, Araldite EPN 1179, Araldite EPN 1180, Araldite EPN 9880, Araldite GY 281, Araldite GY 282, Araldite GY 285, Araldite GY 308, Araldite LY 9703, Araldite PY 307, and Araldite XD 4995, and Tactix 785 (Ciba Specialty Chemicals Corporation trademarks), and Epalloy 8230, Epalloy 8240, 10 Epalloy 8250, Epalloy 8330, and Epalloy 8350 (CVC Specialty Chemicals trademarks).

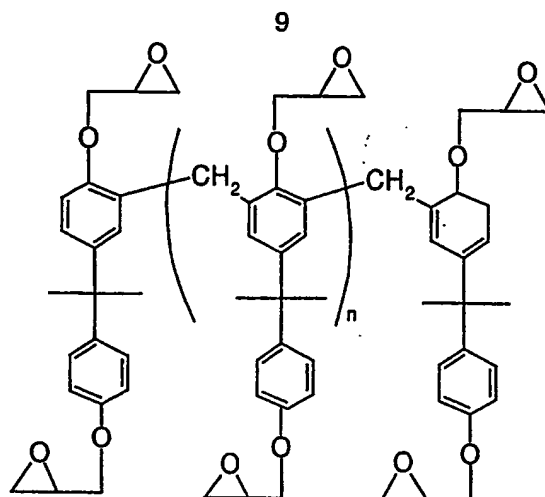
2B Epoxy Cresol Novolacs of the formula:



15 where  $n>0$  can be used.

Epoxy Cresol Novolacs are available from a number of different manufacturers in a variety of molecular weights and viscosities. Examples include: Epon 164 and Epon RSS-2350 (Shell trademarks), and Araldite ECN 1235, Araldite ECN 1273, Araldite ECN 1280, Araldite ECN 1282, Araldite ECN 1299, 20 Araldite ECN 1400, Araldite ECN 1871, Araldite ECN 1873, Araldite ECN 9511 and Araldite ECN 9699 (Ciba Specialty Chemicals Corporation trademarks).

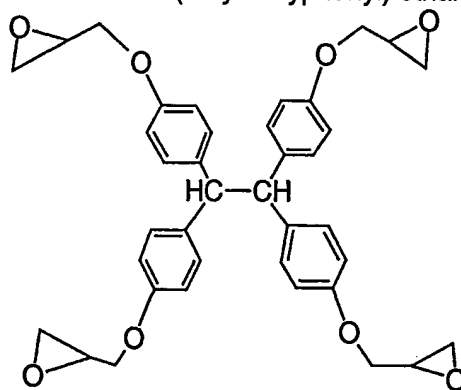
2C. Bisphenol A Epoxy Novolacs of the formula:



where  $n=0$  to about 2 or more.

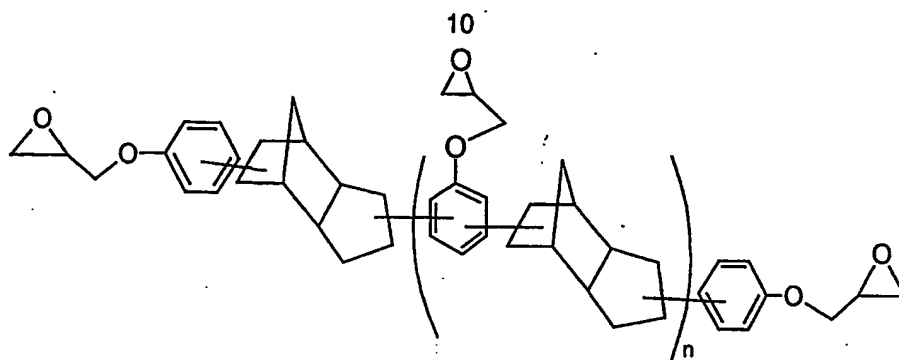
Bisphenol A epoxy novolacs are commercially available in a variety of molecular weights and viscosities as the SU series of resins (Shell Chemical trademark).

3. Tetraglycidyl ether of tetrakis (4-hydroxyphenyl) ethane of the formula:



This is commercially available as Epon 1031 (Shell Chemical trademark) and Araldite MT 0163 (Ciba Specialty Chemicals Corporation trademark).

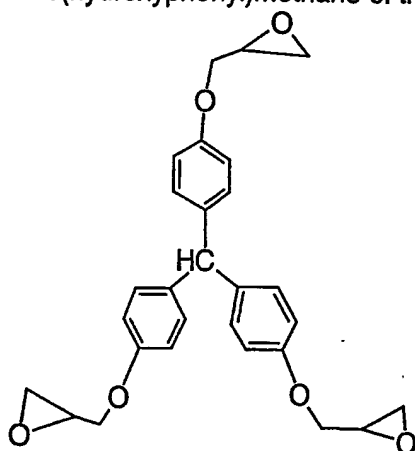
4. Glycidyl ethers of the condensation product of dicyclopentadiene and phenol of the formula:



This product is commercially available as Tactix 556 (Ciba Specialty Chemicals Corporation trademark) where  $n$  is approximately 0.2.

5

5. Triglycidyl ether of tris(hydroxyphenyl)methane of the formula:

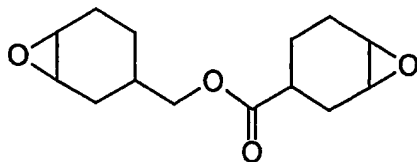


This product is available as Tactix 742 (Ciba Specialty Chemicals Corporation trademark).

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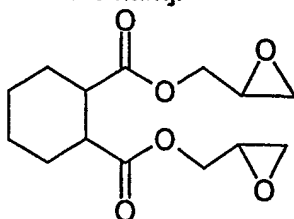
The forgoing epoxy materials can be used alone or as mixtures of several of the materials.

15 The epoxy resin used in the process of the present invention may also contain the following cycloaliphatic epoxides of the indicated formulas, either as the main ingredient of the binder formulation or as a diluent:

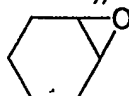


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- 3',4'-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate  
 [available as ERL-4221, Cyacure UVR-6110 and UVR 6105 (Union Carbide Corporation trademarks), Araldite CY-179 (Ciba Specialty Chemicals Corporation trademark), Uvacure 1500 (UCB Chemicals trademark) and as Celloxide 2021 (Daicel Chemical Industries Ltd. trademark)].

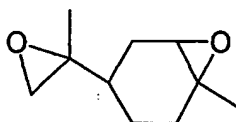


Diglycidyl ester of hexahydrophthalic anhydride (available as CY 184 Ciba Specialty Chemicals Corporation trademark)).

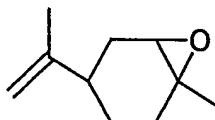


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Cyclohexane oxide.

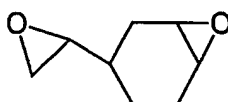


Limonene diepoxide (available as Celloxide 3000 (Daicel Chemical Industries Ltd. trademark)).



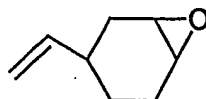
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Limonene monoxide



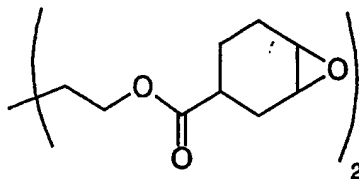
- Vinyl cyclohexene dioxide (available as ERL-4206 (Union Carbide Corporation trademark)).

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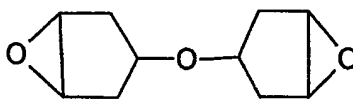


Vinyl cyclohexene oxide (available as Celloxide 2000 (Daicel Chemical Industries Ltd. trademark)).

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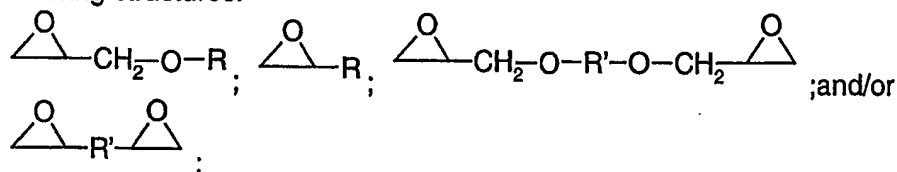
Bis (3,4-epoxycyclohexylmethyl) adipate



Bis (2,3-epoxy cyclopentyl) ether

Other epoxy resins or monomers which can be used in the EB process aspect of the present invention include 2-(3,4-Epoxy cyclohexyl 5,5-spiro-3,4-epoxy) cyclohexane-metadioxane (available as ERL-4234 (Union Carbide Corporation trademark)), epoxycyclohexanecarboxylate modified  $\beta$ -caprolactone (available in various molecular weights as Celoxide 2081, Celoxide 2083, and Celoxide 2085 (Daicel Chemical Industries Ltd. trademarks)), (3,4-Epoxy cyclohexyl) methyl acrylate (available as Cyclomer A-200 (Daicel Chemical Industries Ltd. trademark)), and (3,4-Epoxy cyclohexyl) methyl methacrylate (available as Cyclomer M-100 (Daicel Chemical Industries Ltd. trademark)). These materials can also be used alone or as mixtures.

The epoxy resins can also include polymers with pendent epoxy or cycloaliphatic epoxide groups. The epoxy resin may also include those from the epoxides of the following structures:



wherein R is a monovalent radical, which include a linear, cyclic or branched alkyl group having up to about 18 carbon atoms, e.g., butyl, heptyl, octyl, 2-ethyl hexyl or cyclohexyl; an aryl group e.g., phenyl or alkyl-phenyl such as, for example, cresyl, t-butyl phenyl and nonylphenyl; and an alkenyl group such as allyl. R' is a bivalent radical which include linear or branched alkylene groups having up to about 18 carbon atoms, oxyalkylene groups having, for example, the following



formulae  $(\text{CH}_2\text{CH}_2\text{O})_n$   $(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n$  and the like, where n may be, for example, 1 to about 10.

5 These materials are commonly used, and commercially available epoxy reactive diluents and functional modifiers. Specific examples of these materials may be found in Handbook of Composites, Edited by George Lubin, Van Nostrand Reinhold Company, Inc., New York, N.Y. (1982), pages 61 to 63, and Shell Chemical Company technical brochure SC-1928-95, HELOXY® Epoxy Functional Modifiers.

10

Certain of the epoxy materials are either high viscosity liquids or solids at room temperatures. Therefore, it is contemplated that the higher viscosity materials may be blended with lower viscosity epoxy materials or with reactive or non-reactive diluents in order to achieve the desired viscosity for ease in handling and processing. Heating may be required to achieve the desired flow properties of the uncured formulation but temperatures should not be sufficiently high to cause thermal curing of the epoxy group. Specific blends have been found to have a good overall combination of low viscosity in the uncured states and high glass transition temperature, flexural strength and modulus when cured. One blend which can be mentioned is a high performance semi-solid epoxy such as Tactix 556 with lower viscosity bisphenol A or bisphenol F based glycidyl ether epoxies such as Tactix 123 or Epon 861, respectively.

25 Examples of suitable monomers, oligomers and polymers having at least one or more vinyl ether groups include those of the following general formula:



where

n is an integer from 1 to 4

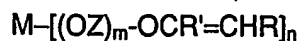
30 R and R' are each, independently H or  $\text{C}_{1-8}$  alkyl,

Z' is a direct bond or a divalent moiety having 1-20 carbon atoms selected from the group consisting of alkylene, cycloalkylene, or polyalkylene ether moieties; and

B is hydrogen or a moiety derived from aromatic and aliphatic hydrocarbons, alcohols, cycloaliphatic hydrocarbons, esters, ethers, siloxanes, urethanes, and carbonates, each containing from 1 to 40 carbon atoms.

Examples of vinyl ethers usable in the process of the first aspect of the present invention are generally defined by the following formulae:

a) Vinyl ether terminated aliphatic monomers of the formula



5 where

n is 1 to 4,

m is 0 to 5,

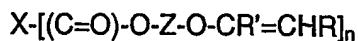
M is a mono, di, tri, or tetra functional aliphatic or cycloaliphatic moiety having from 1-40 carbon atoms;

10 Z is a divalent moiety having 1-20 carbon atoms selected from the group consisting of alkylene, cycloalkylene or polyalkylene moieties; and

R and R' are each, independently, H or C<sub>1-8</sub> alkyl.

b) Vinyl ether terminated ester monomers of the formula

15



where

n is 1 to 4,

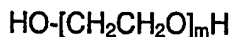
20 X is a mono, di, tri, or tetra functional moiety having from 1-18 carbon atoms selected from the group consisting of alkylene, arylene, aralkylene and cycloalkylene moieties,

Z is a divalent moiety having 1-20 carbon atoms selected from the group consisting of alkylene, cycloalkylene, or polyalkylene ether moieties, and

25 R and R' are each, independently, a monovalent moiety selected from the group consisting of H and alkyl groups having 1-8 carbon atoms.

c) Vinyl ether terminated ether monomers derived from ether compounds such as

30



wherein

m is 2 to 5.

d) Vinyl ether terminated aromatic monomers of the formula

35



where n is 1 to 4,

15

Y is a mono, di, tri, or tetrafunctional aromatic moiety having 6 to 40 carbon atoms;  
and

Z, R' and R" are as defined above.

- 5 e) Vinyl ether terminated siloxane monomers of the formula:

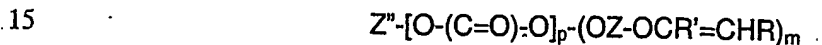


where

n is 1 to 4

- 10 A is a polysiloxane with from 2 to 50 silicon atoms; and  
R, R' and Z' are as defined above.

- f) Vinyl ether terminated carbonate monomers of the formula:



where

m is 1 to 4,

Z'' is a diester, diol or polyol moiety of from 2 to 20 carbon atoms,  
p is 0 to 3, and

- 20 R, R' and Z are as defined above.

Common vinyl ether monomers, oligomers and polymers which are suitable in the process of the present invention include ethyl vinyl ether, propyl vinyl ether, isobutyl vinyl ether, octadecyl vinyl ether, hydroxybutyl vinyl ether, propenyl ether  
25 of propylene carbonate, dodecyl vinyl ether, cyclohexyl vinyl ether, 2-ethylhexyl vinyl ether, butyl vinyl ether, ethyleneglycol monovinyl ether, diethyleneglycol divinyl ether, butanediol monovinyl ether, butane diol divinyl ether, hexane diol divinyl ether, ethylene glycol butyl vinyl ether, triethylene glycol methyl vinyl ether, cyclohexane dimethanol monovinyl ether, cyclohexane dimethanol divinyl ether, 2-ethylhexyl vinyl ether, poly-THF divinyl ether,  $CRH=CR-[O(CH_2)_4-O]_n-CR=CRH$ ,  
30 pluriol-E-200-vinyl ether,  $CRH=CR-[O-CH_2-CH_2]_n-O-CR=CRH$ , bisphenol A divinylether and the like.

Examples of cyclic ethers which can be used in the present invention include  
35 butylene oxide (oxetane), pentylene oxide, 1,3,5 oxanes and oligomers or polymers having related functional groups.

Reactive diluents may be optionally be employed in the formulations to be cured by the new initiator in an amount of up to about 50 % by weight of the formulation. These include low viscosity epoxides or diepoxides, oxetanes or dioxetanes, low viscosity alcohols, polyols, and/or phenols, vinyl ethers, vinyl monomers, cyclic ethers such as tetrahydrofuran, cyclic carbonates and esters, acrylates and methacrylates, and compounds containing more than one type of reactive functionality in the same molecule.

Solvents may be added to the formulation to adjust the viscosity of the uncured formulation to that desired for application. Generally, but not always, solvents would be removed by evaporation from the applied formulation prior to curing. Solvents can be employed in amounts up to about 90 % by weight of the curable formulation.

Alcohols (0 to about 20 % by weight), polyols (0 to about 50 % by weight) and phenolic compounds (0 to about 50 % by weight) may be added to the formulation to modify the uncured rheology or to improve the cured properties of the subject formulations.

Reactive and non-reactive toughening agents may optionally be employed in an amount of up to about 50 % by weight of the formulation. These agents are used to increase the impact resistance and modulus of the systems to which they are added.

Reactive toughening agents include materials which have functionality which will react under acid catalyzed conditions such as epoxy and/or hydroxy terminated rubbers.

Non-reactive toughening agents include materials which do not have functionality which will react under acid catalyzed conditions, or which will react poorly under such conditions, such as polybutadienes, polyethersulfones, polyetherimides, acrylics, and the like.

Mineral fillers may be added. Such fillers are employed in amounts of up to about 70 % by weight of the formulation. Fillers include calcium carbonate (at some expense of cure speed), alumina oxide, amorphous silica, fumed silica, sodium aluminum silicate, titania oxide, clay, etc. Fillers may be surface treated to increase filling ability, or to enhance adhesion to the epoxy resin or to other

components of the abrasive binder, and/or to improved properties of the cured resin. Nanoparticle fillers of various types may also be employed.

5 Pigments or dyes can also be added to the formulation to achieve a desired color or hue. Such materials may be those which are conventionally employed in the art and are used in amounts of up to about 10 % by weight of the formulation.

10 The polymerizable and/or crosslinkable compositions used in the EB polymerization or crosslinking of the present invention are polymerized or crosslinked by exposing the composition to an electron beam. The typical exposure dose is between 0.1 and 500 kGy. Preferably, the dose is generally between 0.8 and 200 kGy, and most preferably between 50 and 150 kGy. Using less than 0.1 kGy will generally not result in any significant polymerization or crosslinking of the cationic active component. Using more than 500 kGy may result in the degradation of the product formed. It is noted, however, that the exact dose needed to cure a given material will vary and depends on factors such as the particular material being polymerized or crosslinked. Any electron beam generating device can be used, however, factors should be taken into account such as the thickness of the resulting product and the materials used to produce the resulting product. The electron beam generating device should be selected so that it has sufficient power to polymerize or crosslink the material.

25 The cationic active components described above have been previously used in composite materials. A composite material is one which contains a fiber reinforcement material such as, for example, carbon fibers, aramid fibers and glass fibers, which is dispersed within the cationic active component matrix. These reinforcement materials are commercially available. In addition, composites can also be made by impregnating a mat of the fiber material with the resin material. Composites have been used in a wide variety of applications, particularly in applications where materials that are light weight and have a high strength are needed. Examples include aerospace, transportation, sporting goods and infrastructure applications.

35 Conventional methods known to those skilled in the art can be used to fabricate the composites of the present invention. Examples of such methods include filament/tape winding, resin transfer molding, pultrusion and hand lay-up, as well as other known methods. Preferably, the curable matrix is an epoxy resin material,

a vinyl ether containing resin or an oxetane containing resin, such as those resin components described above.

5 In curing the resin material used in the composite, care must be taken to ensure that the resin is cured. Electron beam irradiation to cure composite materials can be used so long as the thickness of the composite material is not too thick. This is because the electron beam can only penetrate a certain distance into the composite material. The penetration distance is a function of the electron beam energy and the density of the composite material. However, it is noted that  
10 methods are known to those skilled in the art to overcome the limits of the electron beam, including exposing two sides of the composite material to be cured to the electron beam and using a higher energy electron beam.

15 Photoresist materials typically comprise a resin binder and a photoactive component. In the photoresist materials of the present invention, the photoactive component is the onium gallate compounds described above. For a resin binder to be useful in a photoresist, the binder must typically contain polar groups which impart aqueous alkaline developability to the photoresist composition and the resin must be present in the material in an amount to render the resist material  
20 developable with an aqueous alkaline solution. Examples of the polar groups include hydroxy or carboxylate groups.

Any resin used in conventional photoresist materials can be used in the present invention. Preferred resins include phenolic resins. The phenolic resins which can  
25 be used in the photoresist of the present invention are known to those skilled in the art and include, for example, phenol aldehyde condensates, poly(vinylphenols), copolymers of phenol and nonaromatic cyclic alcohol units, bis-hydroxymethylated compounds and block novolak resins. Such resins are described in U.S. Patent 5,731,364, which is hereby incorporated by reference.

30 In positive photoresist compositions, the resin material contains a group which is acid labile either in a side chain or in the resin backbone. Examples of acid labile groups include acetate groups, such as t-butyl acetate, oxycarbonyl groups, such as t-butyl oxycarbonyl (t-Boc), acetals and ketals. These groups, in the presence  
35 of the acid generated by exposing the onium gallate photoinitiator of the present invention to an energy source, e.g., UV radiation, electron beams, gamma radiation, etc., are converted back to the hydroxy groups. The presence of the hydroxy groups in the exposed portion of the resin render the resin material soluble

in an aqueous alkaline solution. This allows the exposed portion of the resin to be removed from the substrate to which it is applied. The portion of the resin which is not exposed to the energy source is not soluble in the alkaline solution due to the presence of the acid labile groups remaining intact on the resin.

5

In a negative resist material, an additional component is present in the resist composition. The additional component is a crosslinking agent which reacts with the soluble functional groups of the resin to be reacted. Therefore, the exposed portion of the photoresist material is not soluble in the alkaline developing solution and the unexposed portion of the resin is soluble in the alkaline developing solution.

10

Examples of crosslinking agents useable in negative photoresist material include amine- based material such as melamine, benzoguanamine based materials and urea based materials. Other crosslinking agents known to those skilled in the art can also be used.

15

Photoresist relief images are formed on substrates by applying the photoresist material to the substrate, followed by exposing the photoresist coating to a patterned activating radiation and developing the exposed photoresist layer to provide a relief image. The photoresist film may be applied to the substrate using any conventional methods known to those skilled in the art including liquid coating and dry film coating. The substrates which can be provided with a relief image include microelectronic wafers, such as silicon, silicon dioxide and others conventionally used in the microelectronic industry; and flat panel display substrates such as flat panel liquid crystal displays.

20

25

Broadly the present invention comprises a process for polymerizing or crosslinking a cationic polymerizable or crosslinkable component, said process comprising: forming a composition containing a component which is capable of cationic polymerizing or cationic crosslinking and an onium salt having an anion of the formula  $GaX_aR_b$  wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4; and exposing the composition to an electron beam.

30

35

The onium salts may contains a cation selected from the group consisting of iodonium, pyrylium, thiapyrylium, sulphonium, phosphonium, ferrocenium, and diazonium ions,

- 5 Preferably the cation is an iodonium cation, more preferably a diaryliodonium cation, most preferably 4-octyloxyphenylphenyl iodonium.

Preferably the cation is a sulfonium cation, more preferably a triaryl sulfonium cation; most preferably a dialkylphenylacyl sulfonium cation.

10

Preferably the anion is selected from the group consisting of  $[\text{Ga}(\text{C}_6\text{F}_5)_4]^-$ ,  $[\text{Ga}(\text{C}_6\text{H}_4\text{CF}_3)_4]^-$ ,  $[(\text{C}_6\text{F}_5)_2\text{GaF}_2]^-$ ,  $[(\text{C}_6\text{F}_5)\text{GaF}_3]^-$  and  $[\text{Ga}(\text{C}_6\text{H}_3\text{F}_2)_4]^-$ ; more preferably is  $\text{Ga}(\text{C}_6\text{F}_5)_4]^-$ .

- 15 Preferably in the process of the present invention, the composition is exposed to a radiation dose between about 0.8 to about 200 kGy, more preferably from about 50 to about 50 kGy.

20 In a further aspect of the present invention broadly there is provided a composite composition containing a cationic crosslinkable resin, a fiber reinforcement (optionally carbon fibers, aramid fibers, glass fibers or mats thereof) and an onium salt having an anion of the formula  $\text{GaX}_a\text{R}_b$  wherein X is a halogen atom or a hydroxy group, R is an aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4.

25

In a still further aspect of the present invention broadly there is provided a method of preparing a composite, comprising exposing the composite composition of the present invention to an electron beam.

- 30 In a yet further aspect of the present invention broadly there is provided a photoresist composition comprising: a resin binder; and a photoactive component in an amount sufficient to permit development of an exposed coating layer of the composition, wherein the photoactive component is an onium gallate or gallates of organometallic complexes which are cationic initiators for polymerization.
- 35 salt having an anion of the formula  $\text{GaX}_a\text{R}_b$  wherein X is a halogen atom or a hydroxy group, R is an aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4.



The photoresist composition of the present invention may be a negative-acting or positive-acting photoresist (in which case the resin may comprises an acid labile group).

- 5 Preferably the resin binder is a phenolic resin.

In a yet still further aspect of the present invention broadly there is provided an article of manufacture having at least one surface coated with the photoresist composition of the present invention. It will be appreciated that the surface of the  
10 article may be entirely or partially coated (e.g. partially coated in a designated pattern thereon).

In another aspect of the present invention broadly there is provided method of forming a photoresist relief image on a substrate comprising applying a coating  
15 composition containing the photoresist composition of the present invention on a substrate; and exposing the photoresist coating to a patterned activating radiation and developing the exposed photoresist layer to provide a relief image.

20 Preferably the activating energy (or radiation) is X-rays, gamma rays, and/or an electron beam, more preferably an electron beam.

Preferably the substrate is a microelectronic wafer or a flat panel display substrate.

25 In order to illustrate the present invention, the following examples are provided. It is understood that the Examples are not to be construed to limit the disclosed invention.

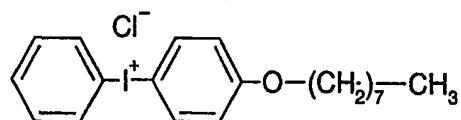
Reference Example 1 (Preparation of Lithium Tetrakis(pentafluorophenyl) gallate)

30 A 125 ml four-necked round bottom flask, equipped with a thermometer and two dropping funnels and a magnetic stirrer, is employed. The assembly was dried under an argon atmosphere. 80 ml of anhydrous pentene and 3.2 ml of bromopentafluorobenzene (25.67 mmol) were charged therein and then cooled to -78C. 10 ml of a 2.5M solution of n-butyllithium (25.04 mmol) in hexane were  
35 added dropwise over one hour. The mixture was maintained under stirring for 3 to 5 hours at -78C. 10 ml of a solution of gallium chloride (6.25 mmol) in benzene (5.6g of GaCl<sub>3</sub> dissolved in 50 mL benzene under an argon atmosphere) were added dropwise to the mixture over one hour. The mixture was kept at -78C for 3

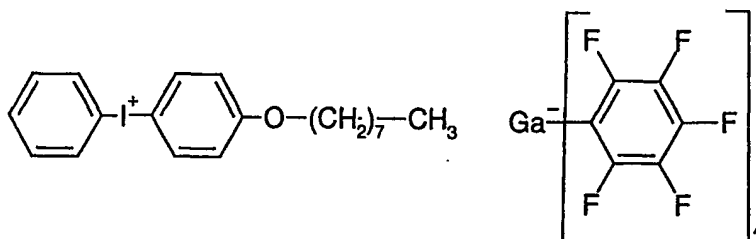
to 5 hours, then the cooling bath was removed. The reaction mixture was allowed to warm to ambient temperature as it was stirred overnight. The mixture was filtered, the filtrate was washed with hexane and then dried under reduced pressure at 60°C. A light yellow solid (containing LiCl) was obtained which has a melting point > 300°C. The product was characterized by <sup>19</sup>F-NMR (DMSO).

Reference Example 2 (Preparation of Iodonium Tetrakis(pentafluorophenyl)gallate)

In a 50 ml round-bottom flask, Lithium Tetrakis(pentafluorophenyl) gallate prepared in accordance with Reference Example 1 is dissolved in 15 ml CH<sub>2</sub>Cl<sub>2</sub>. An equal molar amount of iodonium chloride having the formula:



in 15 ml CH<sub>2</sub>Cl<sub>2</sub> was added dropwise with stirring at room temperature. The reaction mixture became cloudy. After stirring for two hours, the solvent was removed to yield a sticky residue. Chromatography on neutral alumina (a column of 3-5 cm in length was used) by elution with CH<sub>2</sub>Cl<sub>2</sub> gave the iodonium tetrakis(pentafluorophenyl)gallate of the formula:

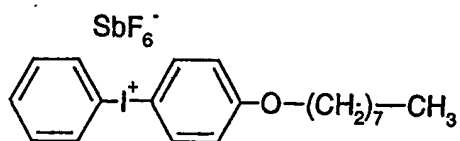


as a yellow sticky liquid. The yield was determined to be about 70 to about 85%. The structure was confirmed by <sup>1</sup>H-NMR and <sup>19</sup>F-NMR.

Examples 1-6 and Comparative Examples 1-2

A portion of a batch of a bisphenol A epoxy resin (DER-332 manufactured by Dow Chemical) and having a molecular weight of about 340g/mole and an epoxy equivalent of about 170g, was divided into 8 aliquots. Each of the aliquots was blended with an amount of an initiator indicated in Table 1, to form the test samples. Initiator A is the initiator prepared in accordance with Reference Example 2 above. Initiator B is octyloxyphenylphenyliodonium

hexafluoroantimonate (OPPI) which is available from GE Silicones and has the formula:



5 The samples were heated to about 60 C for about 2 hours to dissolve the initiator in the epoxy resin.

Table 1

Example No.	Initiator	Amount of initiator in sample wt. %
1	A	1.0
2	A	0.5
3	A	0.25
4	A	1.0
5	A	0.5
6	A	0.25
Comparative Ex. 1	B	1.0
Comparative Ex. 2	B	0.502

Each of the samples of the Examples is divided into separate sets and tested as follows:

- 10 A first set of samples were exposed to gamma radiation from a Cobalt 60 gamma radiation source to determine the temperature rise, the gel point and the energy needed to result in a 50% cure. The temperature rise is a measurement of the exothermicity of the reaction. The higher the temperature rise generally indicates an efficient polymerization reaction. The gel point is a measurement of the
- 15 minimum radiation dose needed to cure the composition. The results are shown in Table 2.

Table 2

Example No.	Temp. Rise °C	Gel Point (kGy)	50% Cure (kGy)
1	18	0.8	4.5
2	13	0.8	4.9
3	6	0.8	6.2
4	7	0.8	3.7
5	10	0.8	4.5
6	5	0.8	5.2
Comp. Ex. 1	10	0.9	4.3
Comp. Ex. 2	9	0.9	4.5

A second set of the samples were subject to curing using an electron beam. The samples were cured for the purpose of dynamic mechanical analysis (DMA) tests.

- 5 The uncured samples were drawn into a syringe of about 1ml each. Next the samples were irradiated using a 1-10/1 electron accelerator. A 10 MeV pulsed electron beam was configured with a vertical horn to scan over a 30 cm wide path onto a variable speed conveyor belt. The instantaneous dose rate delivered during a pulse was 530 kGy per second. The dose deposited per pass under the beam
- 10 was 25 kGy per pass. A total dose of 150kGy absorbed the material was delivered by accumulating 6 successive passes under the beam. Each of the samples, once cured, are subjected to DMA testing. Results of the (DMA) tests are in Table 3.

Table 3

Example No.	Flexural Modulus (GPa)	Service Temperature	T <sub>g</sub> °C (loss modulus)	T <sub>g</sub> °C (tan δ)
1	2.50	150	190	207
2	2.30	160	195	212
3	2.43	158	180	207
4	2.33	158	190	207
5	2.45	160	193	210
6	2.02	160	185	212
Comp. Ex. 1	2.79	137	153	202
Comp. Ex. 2	2.81	100	108	135

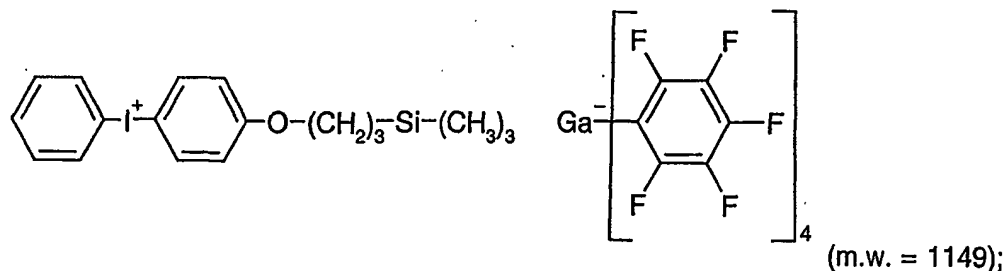
5 The flexural modulus was measured at room temperature after curing. The service temperature is the temperature in which modulus is one-half the modulus measured at 25°C. The  $T_g$  is the glass transition temperature of the cured resin, and is reported as a function of the loss modulus and as a function of the peak in the tan delta plot.

10 As can be seen in Table 3, the epoxy resin cured using an electron beam and the onium gallate of the present invention results in a cured resin having improved physical properties over the same resin cured with a conventional onium salt available in the art. Further, it can be seen that less of the initiator is need to cure the samples when the initiator of the present invention is used. These results suggest that the onium gallate of the present invention is very effective for curing cationic compositions as compare to another commercially available onium salt  
15 having the same cation.

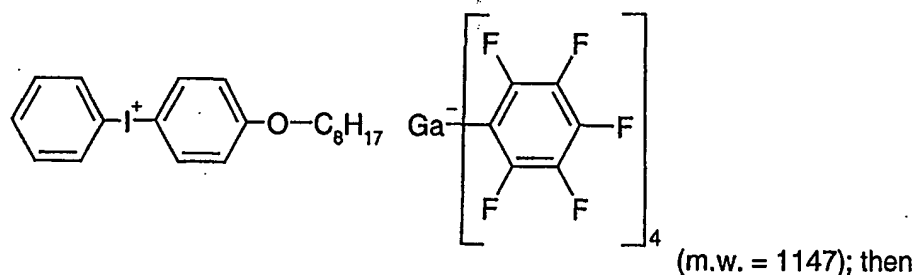
The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modifications can be made without departing from the scope or spirit of the invention as set forth in the following claims.  
20

CLAIMS

1. A process for polymerizing or cross-linking a cationic polymerizable or cross-linkable component, said process comprising
- 5 a) forming a composition containing a component which is capable of cationic polymerizing or cationic cross-linking and an onium salt having an anion of the formula  $\text{GaX}_a\text{R}_b$  wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4; and
- 10 b) exposing the composition to radiation selected from the group consisting of actinic radiation, X-rays, gamma-rays and an electron beam;
- with the proviso that when cross-linkable or polymerizable component is a matrix of the diglycidyl ether of bisphenol-A available commercially from Dow Chemical under the trademark DER 332; and the onium salt is present in an
- 15 amount of 1% by weight of the composition and is either:



or



- the composition is exposed to radiation other than an electron beam at a beam
- 20 voltage of 200mV and a dose of 10 Mrad.

2. A process for polymerizing or cross-linking a cationic polymerizable or cross-linkable component, said process comprising
- a) forming a composition containing a component which is capable of
- 25 cationic polymerizing or cationic cross-linking and an onium salt having an anion of

27.

the formula  $\text{GaX}_a\text{R}_b$ , wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4; and

5 b) exposing the composition to a dose of activating radiation to cross-link and/or polymerize the composition, such that the resultant composition has at least one of the following properties:

- i) a flexural modulus of less than about 2.5 Gpa;
- ii) a service temperature of greater than about 150°C;
- 10 iii) a  $T_g$  (measured as a function of the loss modulus) of greater than about 180°C; and/or
- iv) a  $T_g$  (measured as a function of the peak in a tan delta plot) of greater than about 207°C.

3. The process of claim 2, where the radiation is selected from the group  
15 consisting of UV, actinic radiation, X-rays, gamma-rays and an electron beam.

4. The process of any preceding claim, where the onium salt contains a cation selected from the group consisting of iodonium, pyrylium, thiapyrylium, sulphonium, phosphonium, ferrocenium, and diazonium ions.  
20

5. The process of claim 4, where the cation is an iodonium cation.

6. The process of claim 5, where the iodonium cation is a diaryliodonium cation.  
25

7. The process of claim 6, where the diaryliodonium cation is 4-octyloxyphenylphenyl iodonium.

8. The process of any preceding claim, where the cation is a sulfonium cation.  
30

9. The process of claim 9, where the sulfonium cation is selected from a triaryl sulfonium cation and/or a dialkylphenylacyl sulfonium cation.

10. The process of any preceding claim, where the anion is selected from the  
35 group consisting of  $[\text{Ga}(\text{C}_6\text{F}_5)_4]^-$ ,  $[\text{Ga}(\text{C}_6\text{H}_4\text{CF}_3)_4]^-$ ,  $[(\text{C}_6\text{F}_5)_2\text{GaF}_2]^-$ ,  $[(\text{C}_6\text{F}_5)\text{GaF}_3]^-$ , and  $[\text{Ga}(\text{C}_6\text{H}_3\text{F}_2)_4]^-$ .

11. The process of claim 10, where the anion is  $[\text{Ga}(\text{C}_6\text{F}_5)_4]^-$ .
12. The process of any preceding claim, where the onium salt is substantially dissolved in the polymerizable or cross-linkable component.
- 5 13. The process of any preceding claim, where the onium salt is added in an amount from about 0.25% to about 0.5% by weight of the composition.
- 10 14. The process of any preceding claim, where the composition is exposed to a radiation dose between about 0.8 and about 200 kGy.
- 15 15. The process of claim 14, where the dose is between about 50 and about 150 kGy.
16. The process of any preceding claim, where the radiation dose applied to produce a 50% cure of the composition is less than or equal to about 6.2 kGy.
17. The process of claim 16, where the radiation dose applied to produce a 50% cure is from about 4.5 kGy to about 6.2 kGy.
- 20 18. The process of any preceding claim, where minimum radiation dose required to initiate cure of the composition (gel point) is less than or equal to about 0.8 kGy.
- 25 19. The process of any preceding claim which comprises an exothermic reaction.
20. The process of claim 19, in which the reaction temperature rises by at least 5°C.
- 30 21. A composition obtained and/or obtainable by the process of any preceding claim which has at least one of the following properties:
- i) a flexural modulus of less than about 2.5 Gpa;
  - ii) a service temperature of greater than about 150°C;
  - 35 iii) a  $T_g$  (measured as a function of the loss modulus) of greater than about 180°C; and/or



iv) a  $T_g$  (measured as a function of the peak in a tan delta plot) of greater than about 207°C.

22. The composition of claim 21, which has at least one of the following properties:

- i) a flexural modulus of from about 2.0 to about 2.5 GPa;
- ii) a service temperature of from about 150°C to about 160°C;
- iii) a  $T_g$  (measured as a function of the loss modulus) of from about 180°C to about 195°C; and/or
- iv) a  $T_g$  (measured as a function of the peak in a tan delta plot) of from about 207°C to about 212°C.

23. A composite composition containing a cationically cross-linkable resin, a fiber reinforcement and an onium salt having an anion of the formula  $GaX_aR_b$  wherein X is a halogen atom or a hydroxy group, R is an aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4.

24. The composite composition according to claim 23, where the fiber reinforcement is carbon fibers, aramid fibers, glass fibers or mats thereof.

25. A photo-resist composition comprising  
a resin binder and  
a photo-active component in an amount sufficient to permit development of an exposed coating layer of the composition, and where  
the photo-active component is an onium gallate or gallates of organometallic complexes which are cationic initiators for polymerization, said salt having an anion of the formula  $GaX_aR_b$  wherein X is a halogen atom or a hydroxy group, R is an aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4.

26. The photo-resist composition of claim 25, where the composition is a negative-acting photo-resist.

27. The photo-resist composition of claim 25, where the composition is a positive-acting photo-resist.

28. The photo-resist composition of any of claims 25 to 27, where the resin binder is a phenolic resin.

5 29. The photo-resist composition of any of claims 25 to 28, where the resin comprises an acid labile group.

10 30. A method of preparing a composite, comprising exposing the composite composition of claim 23 or 24, to radiation selected from the group consisting of actinic radiation, UV, X-rays, gamma-rays and an electron beam.

15 31. A method of forming a photo-resist relief image on a substrate comprising applying the photo-resist composition of any of claims 25 to 29 on a substrate to form coating thereon ; and exposing the photo-resist coating to a patterned activating radiation and developing the exposed photo-resist layer to provide a relief image.

20 32. The method of claim 31, wherein the activating energy is selected from the group consisting of actinic radiation, UV, X-rays, gamma-rays and an electron beam.

33. The method of claim 31 or 32, wherein the substrate is a micro-electronic wafer or a flat panel display.

25 34. An article of manufacture having at least one surface coated with the composition of any of claims 21 to 29.

35. The article of claim 34, which is a micro-electronic wafer or a flat panel display.

30 36. Use of an onium salt as an initiator for cationic cross-linking and/or polymerization of a composition with activating radiation, where the onium salt has an anion of the formula  $GaX_aR_b$  wherein X is a halogen atom or a hydroxy group, R is an aryl group or a substituted aryl group, a and b are each represent an integer of 0 to 4 provided that the sum of a and b is 4;

the composition comprises a component which is capable of cationic polymerization and/or cross-linking to form after irradiation a cured composition having at least one of the following properties:

- i) a flexural modulus of less than about 2.5 GPa;
- 5 ii) a service temperature of greater than about 150°C;
- iii) a  $T_g$  (measured as a function of the loss modulus) of greater than about 180°C; and/or
- iv) a  $T_g$  (measured as a function of the peak in a tan delta plot) of greater than about 207°C.